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AN ELEMENTARY TREATISE
ON HEAT.

AN ELEMENTARY TREATISE ON HEAT.

AN ELEMENTARY TREATISE ON HEAT

IN RELATION TO

STEAM AND THE STEAM-ENGINE.

BY

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PREFACE.

THIS book is intended to give an elementary account of the dynamical theory of heat as applied to the expansion of gases and vapours, which shall be intelligible without any previous knowledge of the Differential and Integral Calculus.

It is based almost exclusively on three works, namely:

i. Rankine's *Manual of the Steam-Engine.*

ii. Zenner's *Grundzüge der Mechanischen Warmëtheorie,* (of which there is a French Translation), and

iii. Clerk Maxwell's *Theory of Heat.*

The last of these treats of the whole theory of heat and its historical development in an elementary manner, but more from a scientific than an engineering point of view.

The two former, while written for engineers, cannot be read by one who is not familiar with the Calculus.

It is hoped that this book will prove itself adapted to the wants of engineering students who may not be able to follow the reasoning of Rankine and Zenner.

LEVEN, *Feb.* 1877.

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CHAPTER I.

GENERAL DESCRIPTION OF THOSE EFFECTS OF HEAT WHICH ARE TO BE CONSIDERED AND A METHOD FOR THEIR GRAPHIC REPRESENTATION.

1. **Heat and Energy.** Heat is a form of energy residing in all substances, which energy can under certain conditions be transformed into external work; on the other hand, work expended in certain ways produces, or is transformed into, heat.

Our object here is to investigate the more important laws of the transformation of the energy of heated substances into external work, when those substances are fluids either wholly or partly in the gaseous state.

These laws have a special interest, because it is upon such a transformation that the working of the steam-engine depends.

Since heat and work are convertible forms of the same energy, therefore quantities of heat may properly be expressed in terms of the quantities of external work to which they are equivalent.

2. **Unit of work.** The unit which we shall apply for the measurement of work, and therefore also of heat, is the foot-pound; that is to say, the quantity of work expended

in moving a mass of one pound through a distance of one foot against the action of a constant force whose intensity is equal to the mean force of gravity.

3. **Classification of Phenomena.** The effects of heat which we are to consider may conveniently be divided into three classes, namely, the phenomena of Sensible Heat, of External Work, and of Internal Work.

4. **Sensible Heat.** All heated bodies have a tendency to communicate heat to other bodies within their influence, and to receive heat from them in return.

The condition that determines which of these tendencies shall predominate is called *Temperature.*

In the interchange of heat between two bodies, if there be thermal equilibrium so that each receives back as much heat as it gives out to the other, and, on the whole, neither of them gains or loses by its communication with the other, then the two are said to be at the same temperature.

If one body loses heat which the other gains, the former is said to be at the higher and the latter at the lower temperature.

Heat cannot be transferred from one body at a lower to another at a higher temperature, except by the aid of a machine and the expenditure of mechanical force.

When a body gains a sufficient quantity of heat its temperature tends to rise, and when it loses heat in sufficient quantity the temperature tends to fall.

Thus, when two bodies at different temperatures are brought into communication and left to themselves, the transfer of heat from the body at the higher to that at the lower temperature will continue until, either by the lowering of the temperature of the former, or the rise of the temperature of the latter, or by both processes, thermal equilibrium is reached, and the bodies are brought to the same temperature.

Our senses are directly affected by differences of temperature, and hence that part of the energy of a heated substance which manifests itself in raising the temperature is spoken of as *Sensible Heat.*

The sensations thus produced are not capable of having definite numerical values assigned to them, and it would be impossible to construct a scientific theory of heat from them alone.

5. **External Work.** Heat, however, has other phenomena besides those of temperature; for instance, when heat is communicated to any substance, it tends to produce a change of volume; or, if the substance be so confined that the volume cannot alter with sufficient freedom, the heat supplied produces an alteration in the pressure of the substance against the confining structure. It is on these circumstances that all our present calculations are based.

A few substances have their volumes diminished, under certain circumstances, by the communication of heat; the most noteworthy example of this being, that when ice is converted into water by heat, the volume diminishes, and the water itself continues to decrease in volume as more heat is supplied to it, until its temperature has been raised to a point somewhat above the temperature of melting, after which it again expands.

In the majority of cases, however, and in all those which we are about to investigate, the communication of heat to a substance tends to increase its volume; or, if that cannot expand with sufficient freedom, causes an increase of pressure.

By observations of these changes of pressure and volume differences of temperature also are measured; some of the different systems of measurement will be described later on.

When a substance expands against pressure it performs work, whose amount in foot-pounds is found by multiplying the amount of the pressure in pounds into the distance in feet through which the point of application of that pressure is forced back.

Thus, when the energy of heat is spent in causing expansion against pressure, it is converted into *External Work.*

Of course, energy which has been so transformed no longer exists in the substance in the form of heat, and therefore cannot affect its temperature.

6. **Internal Work.** The energy which does remain in the substance, does not all necessarily show itself in the form of Sensible Heat by affecting the temperature.

A part of the energy of heat in every known substance is expended in producing molecular changes other than those upon which the temperature directly depends.

Such energy is said to be absorbed in performing *Internal Work.*

In some cases these molecular changes make an entire change in the physical constitution of the substance, as when ice becomes water by fusion, or when water becomes steam by evaporation, but in general their results are not so obvious.

7. **Hypothetical Apparatus.** Since we are to investigate the effects of Heat upon fluids wholly or partly gaseous, by means of calculations based upon the measurement of their pressures and volumes, it will be well to have ideas of such measurements as simple and definite as possible.

With a view to this let us suppose one pound weight of such a fluid to be enclosed in a cylinder. Let the cylinder be fitted with a piston capable of moving in it without friction, and whose weight is so small that it may be neglected. Let the area of this piston be one square foot, so that the volume of the pound of fluid expressed in cubic feet may be numerically equal to the distance of the piston from the bottom of the cylinder in linear feet. It follows that the pressure of the fluid in pounds per square foot will be sensibly equal to the external pressure on the piston in pounds, so long as this does not alter suddenly.

In order to examine the effects of heat upon the fluid, we will suppose moreover that the piston and sides of the cylinder are impervious to heat, and that the end of the cylinder is formed of a substance through which heat passes without any impediment; but that it also can be made impervious to heat, when necessary, by the application of a cover which will prevent heat from passing in any direction to or from the fluid in the cylinder. Of course, no apparatus fulfilling these conditions can really be constructed, but it is necessary to make some such assumption in order to free our calculations from the disturbing influences which are met with in the actual observation of the effects of heat.

8. **Graphic representation of pressures and volumes.** In order to represent graphically the pressure and volume of the fluid in this cylinder at any given moment, draw two lines *OX*, *OY* (fig. 1) at right angles to one another; on *OX* take a point *M* such that the distance *OM* shall represent according to any given scale the distance of the piston from the bottom of the cylinder in feet; through *M* draw a straight line parallel to *OY*, and on it take a distance *MA* to represent according to any given scale the amount of the external pressure on the piston in pounds. Then, by Art. 7, the distance *OM* represents also the volume of the fluid in cubic feet, and the distance *MA* represents its pressure in pounds on the square foot. Thus the position of the point *A* on the diagram indicates the condition of the fluid with regard both to pressure and volume.

But it is found that with each condition of the pressure and volume per pound of any given fluid there is associated a definite condition in respect of Sensible Heat and of Internal Work; so that the position of the point *A* on the diagram defines in these respects also, the thermal condition of the fluid whose pressure and volume it represents.

In the same way the condition of the fluid at some other time may be represented by the point *B*, and any series of changes undergone in passing from the state represented by the point *A* to that represented by the point *B* may be indicated by a line *APQB*, such that the condition of the fluid at each moment during the changes is represented by a point on that line.

For convenience, we may speak of the state represented by any point *A* or *B* as the state *A* or *B*, and the fluid when undergoing the changes represented by any line *APQB* may be said to change according to that line. Also the series of changes themselves may be termed the operation *APQB*.

9. **Representation of External Work.** The peculiar value of this mode of representing graphically the pressure and volume of the fluid depends upon the results of the following proposition.

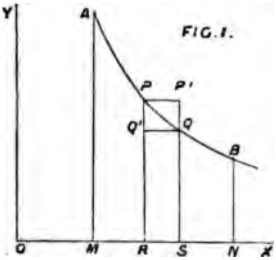


FIG. 1.

The external work done by the fluid during any such operation as APQB *is represented by the area included between the curve* APQB, *the line* OX, *and two straight lines parallel to* OY *drawn through* A *and* B, *the points which represent the initial and final states of the fluid.*

The unit of area employed must be a rectangle, one side of which is a line equal to that which represents the motion of the piston through a distance of one linear foot, and the other side a line representing a change of pressure in the fluid of one pound on the square foot, since the unit of work is the foot-pound.

Through B draw BN parallel to OY to meet OX in N, then the number of such units of area in the area $MAPQBN$ is equal to the number of foot-pounds of external work done by the fluid in the operation $APQB$.

Let the straight line MN be divided into any number of equal parts, and let RS be one of those parts. Through R and S draw RP, SQ parallel to OY to meet the curve $APQB$ in P and Q. Also through P and Q draw PP', QQ' parallel to OX to meet SQ produced, and PR in P' and Q' respectively.

Then the line PP' represents the changes which would take place while the piston moved through the space RS, if the pressure should remain constantly equal to the pressure in the state P.

In this case the external work would evidently be equal to the product of the constant pressure into the space through which the piston moved, and would be represented by the area *RPP'S*. In the same way if the pressure throughout the motion of the piston were equal to that in the state *Q*, then the external work would be represented by the area *RQ'QS*.

The work actually performed in the operation *PQ* is represented by an area intermediate between *RPP'S* and *RQ'QS*.

But if the number of equal parts into which *MN* is divided be indefinitely increased, and the distance *RS* consequently diminished indefinitely, the areas *RPP'S* and *RQ'QS* may be made to differ by a quantity less than any assigned quantity, and to become ultimately equal to one another, and to the area *RPQS*.

Therefore when the distance *RS* is sufficiently small, the work done by the fluid during the operation *PQ* is ultimately represented by the area *RPQS*.

Therefore summing up the amounts of work done by the fluid in driving the piston through the spaces represented by each of the small parts such as *RS* into which *MN* is divided, we find that the total work performed during the whole operation *APQB* is represented by the sum of all the small areas such as *RPQS*, that is to say, by the area *MAPQBN*. From this property such a diagram is called a *Diagram of Energy*.

It is evident that if the changes had taken place in the reverse order, and the fluid had been compressed from the state *B* according to the curve *BQPA* till it was brought to the state *A*, then the same area would represent the work done upon the fluid by the external forces producing the compression.

In order to distinguish between the two cases we may consider areas to have a positive sign when they represent work done by the fluid, and a negative sign when they represent work performed upon the fluid by external forces.

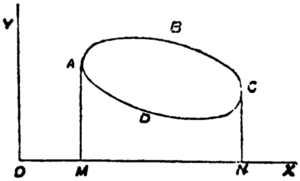
Thus areas will be positive or negative according as the curve representing the operations performed is described from left to right or from right to left.

Since a number of units of work is to be represented by an equal number of units of area, it will be convenient to speak of quantities of work as being 'equal' to the areas representing them.

10. **Cycle of Operations.** When the fluid after undergoing a series of changes returns at last to exactly the same state as that from which it started, the process is called a *Cycle of Operations.*

If in such a cycle the fluid pass through a series of changes, and afterwards return to its original state by passing through the same series in the reverse order, then, on the whole, as much work will have been performed upon the fluid in the second series as was done by it in the first series of changes, and the positive and negative areas will exactly balance one another. If, however, the fluid after passing through one series of changes be brought again to its original state by means of a different series, the cycle of operations will be represented on the diagram of energy by a closed curve.

FIG 2.



Let *ABCD* be such a curve, then if the fluid expand from *A* to *C* according to the curve *ABC*, and be compressed again from *C* to *A* according to the curve *CDA*, the work done by the fluid during the expansion will be represented as before by the area *MABCN*, and the work done upon the fluid by external forces by the area *MADCN*.

Therefore the balance of work given out by the fluid will be represented by the area *ABCD.*

In the same way if the fluid expand according to the curve *ADC*, and be compressed according to the curve *CBA*, so that the cycle is performed in the reverse order, the balance of work expended upon the fluid during the cycle will be represented by the same area *ABCD*, which will then, according to our convention for expressing such work, be considered negative.

CHAPTER II.

GENERAL PROPERTIES OF ADIABATIC AND ISOTHERMAL LINES.

11. **Adiabatic Curves.** Suppose a cylinder, such as that above described, to have the non-conducting cover applied to its end, so that no heat can pass to or from the enclosed fluid, and let the external force acting on the piston be gradually increased, then evidently the volume of the fluid will be diminished, and the series of changes which takes place may be represented by a certain curve on the diagram of energy.

If again the pressure be diminished the same changes will be reproduced in the reverse order, and may be represented by the same curve drawn in the opposite direction.

The general form of this curve may be seen from the consideration that as the pressure increases, the volume must diminish without limit, but can never be actually reduced to nothing; the curve, therefore, gradually approaches nearer to OY as the distance from OX increases, but can never touch OY.

In the same way, since the fluid in the cylinder was supposed to be at least partly in the gaseous state, the pressure will diminish as the volume increases without limit, but we have no reason to suppose that it would ever entirely vanish, so that the curve when produced indefinitely in the other direction continually approaches OX, but can never reach it.

Such a curve representing the changes of pressure and volume which can take place in a fluid when heat is not allowed to pass through the walls of the containing vessel, is called a 'Curve of no Transmission,' or an 'Adiabatic Curve.' (From α, not, and διαβαίνειν, to pass through.)

12. **Intrinsic Energy.** Let *A* and *B* be two points on the indefinitely extended curve $AB\phi$, which is an adiabatic for the fluid contained in our cylinder. Through *A* and *B* draw *AM, BN* parallel to *OY* and meeting *OX* in *M* and *N* respectively.

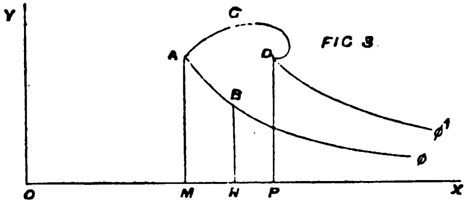


FIG 3.

When the fluid is in the state *A*, it is capable of performing a certain definite quantity of work in virtue of the energy of the heat which it possesses and which causes it to be in the condition represented by the point *A*.

The total amount of this power of doing work is called the *Intrinsic Energy* of the fluid in the state *A*.

In expanding from the state *A* to the state *B* without transfer of heat to or from external sources, the fluid performs a quantity of work equal to the area *MABN*; and since it has not received any additional energy from external sources during the process, its remaining intrinsic energy when in the state *B* must be less than its intrinsic energy in the state *A* by the same amount.

By sufficiently expanding the fluid from the state *A*, according to the adiabatic curve, we may make its remaining intrinsic energy after expansion as small as we please; and at the same time the quantity of work done will become as nearly as we please equal to the area included between the straight line *AM* and the straight line and curve *MNX* and $AB\phi$, when these are indefinitely extended.

Hence the whole work which the fluid is capable of performing in virtue of the heat it possesses in the state *A*, or, in other words, the intrinsic energy of the fluid in the state A, is equal to the indefinitely extended area $XMA\phi$.

It may be as well to remind the reader that an area is not necessarily infinitely large because it is indefinitely extended, but has often a fixed limit which it can never exceed, however far the lines enclosing it be produced. In the present instance there is evidently such a limit, for a fluid cannot be supposed capable of performing an infinite quantity of work in virtue of the heat which it possesses in any given state whatever.

13. **Area representing Heat absorbed.** When the fluid is in the state A, let the non-conducting cover be removed from the end of the cylinder and heat supplied in any manner, causing the fluid to undergo a definite series of operations.

Let these changes be represented by the line ACD on the diagram (fig. 3), and through D, the point representing the final state of the fluid, draw the adiabatic curve $D\phi'$.

Then the total heat absorbed by the fluid during the operation ACD is equal to the indefinitely extended area $\phi ACD\phi'$ enclosed between the curve ACD and the two adiabatics $A\phi$ and $D\phi'$.

For, through D draw the straight line DP parallel to OY to meet OX in P.

The work performed by the fluid during the operation ACD is equal to the area $MACDP$. And the whole work which the fluid in the state D is capable of performing without receiving any farther supply of heat is equal to the area $XPD\phi'$.

Thus the whole work which the fluid, starting from the state A and absorbing heat during the operation ACD, is capable of performing is equal to the area $XMACD\phi'$.

But the fluid in the state A had already the intrinsic energy $XMA\phi$.

Therefore subtracting this from $XMACD\phi'$, we find that the additional energy necessary to render the fluid capable of performing the work $XMACD\phi'$ is equal to the area $\phi ACD\phi'$.

Now the only energy supplied to the fluid in addition to the amount which it possessed in the state *A*, is that which it received in the form of heat during the operation *ACD*.

Therefore the heat absorbed by the fluid during the operation *ACD* is equal to the area $\phi ACD\phi'$.

14. **Isothermal lines.** There is no transfer of heat to or from the fluid during its expansion or compression according to an adiabatic curve, but it must not be supposed from this that the Sensible Heat, and with it the temperature of the fluid, remains constant.

It is found that all gaseous fluids, doing work by expanding against external forces without absorbing heat, have their temperatures lowered in the process.

This indeed might be expected, since energy which existed in the fluid in the form of heat leaves it and becomes transformed into external work during expansion.

Let there be applied to the end of the cylinder a body whose temperature is kept constant. If the external pressure on the piston be now diminished, and the fluid allowed to expand, its temperature will tend to fall, and heat will then flow from this external body to the fluid; and by making the expansion sufficiently gradual we may keep the temperature of the fluid as nearly as we please equal to that of the source of heat. In the same way, if the fluid be compressed, heat will flow from it to the external body, and if the process be gradual, the temperatures of the two may be kept sensibly equal, and the changes undergone by the fluid during compression will be sensibly the same as those which took place during expansion, but in the reverse order.

The line by which these operations are represented on the diagram of energy is called an 'Isothermal Line.' (From *ἴσος*, equal, *θέρμον*, heat, or in this case 'temperature.')

Considerations similar to those from which we found the general form of Adiabatic Curves, show that Isothermal Lines also gradually approach the lines *OX*, *OY*, as the distance from *O* increases, but can never touch them.

Also, since heat is absorbed by a gaseous fluid in expanding according to an isothermal line, therefore its intrinsic energy will not decrease so rapidly as when the expansion takes place according to an adiabatic. Hence at the point where the two curves meet, an isothermal will be more nearly horizontal than an adiabatic.

15. **Carnot's Cycle.** Suppose now that we have two bodies *R* and *S*, which can be kept constantly at two fixed temperatures; *R* being at the lower, and *S* at the higher temperature.

Let the fluid in our cylinder be at the same temperature as the body *R*, and let its state be indicated by the point *A*. Then first let the non-conducting cover be placed on the end of the cylinder and the piston forced down so that the fluid is compressed without transfer of heat till its temperature has risen to that of the body *S*, the operation being represented by the adiabatic curve *AB*.

Secondly, let the cover be removed, the body *S* applied to the end of the cylinder, and the fluid allowed to expand, at the same time absorbing heat from the body *S* so that its temperature remains constant.

Let this expansion be represented by the isothermal line *BC*.

Thirdly, let the non-conducting cover be replaced on the end of the cylinder and the fluid farther expanded from the state *C* to the state *D*, but this time without transfer of heat, according to the adiabatic *CD*, the temperature falling

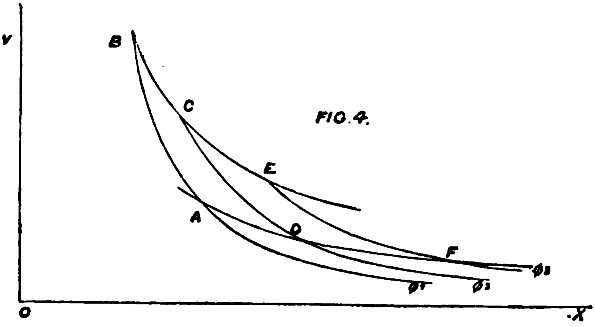


FIG. 4.

in the process till at D it is equal to that of the body R, and therefore the same as in the initial state A.

Lastly, by compressing the fluid, while heat is given out to the body R, so that the temperature may remain constant, it will be possible to complete the cycle, and to bring the fluid back, according to the isothermal DA, to the initial state A.

Such a series of operations is called "Carnot's Cycle," because Carnot first made use of it in calculating the effects of heat.

The body S is referred to as the source of heat, and the body R as the refrigerator.

16. **Reversibility of Carnot's Cycle.** One important property of this cycle is that it is *reversible;* in other words, the very same series of changes can be produced in the reverse order, an amount of work being thus performed upon the fluid, equal to that which was done by the fluid in the original cycle.

This reversing of the cycle could not have been effected if in any part of it heat had been allowed to pass from a body at a higher temperature to another at a sensibly lower one without performing any external work; for, as we have said, the heat could not be returned from the body at the lower temperature to that at the higher one without an expenditure of work, and therefore more work would have to be performed upon the fluid in the reversed cycle, than was done by it in the original one, and the two cycles would not coincide.

If the temperatures of the source of heat and of the refrigerator be constant, 'Carnot's Cycle' and 'a reversible cycle' are equivalent terms, since it is evident that no other cycle could be performed which should have this property.

17. **Quantities of Heat absorbed and rejected in Carnot's Cycle.** In any cycle, since the fluid returns at last to the state from which it started, none of the heat absorbed can be permanently expended in producing changes in the fluid, but all must either be converted into external work, or

rejected in the form of heat. Thus, if the quantity of heat absorbed be *m* foot-pounds, and the heat rejected be *n* foot-pounds, the external work performed must be $(m-n)$ foot-pounds.

Also in a reversible cycle, if the temperatures of the source of heat and the refrigerator be fixed, the ratio of the quantities of heat absorbed and rejected is thereby determined. For if not, let two fluids in passing through reversible cycles with the same source of heat *S* and refrigerator *R*, absorb *m* foot-pounds of heat, but let the first reject *n* foot-pounds, while the second rejects some other quantity of heat.

Let this second fluid now pass through another reversible cycle in which it absorbs as before *m* foot-pounds of heat from *S*, but rejects *n* foot-pounds to the refrigerator, which must therefore be a body at a different temperature from that of *R*. Let *R'* be such a body. We have then two fluids passing through reversible cycles, both receiving *m* foot-pounds of heat from a source *S*, and both rejecting *n* foot-pounds, but the first giving out heat to a refrigerator *R*, and the second to a refrigerator *R'*, where *R* and *R'* are at different temperatures.

Suppose that *R'* is at the higher temperature. Now let the cycle of the first fluid be reversed so that it shall absorb *n* foot-pounds of heat from the body *R* and give out *m* foot-pounds to the body *S*, $(m-n)$ foot-pounds of work being therefore expended on the fluid during the process.

But by supposition the second fluid absorbs from *S*, *m* foot-pounds of heat, the same quantity which the first now rejects, and gives out *n* foot-pounds to the body *R'*; performing in the process a quantity of work equal to that which is expended upon the first fluid.

The result of the supposed operations is therefore that on the whole no work has been expended on the two fluids, and yet *n* foot-pounds of heat have been transferred from a body *R* to another body *R'* at a higher temperature, which is impossible.

Therefore the second fluid cannot in a reversible cycle reject *n* foot-pounds of heat to a refrigerator at any other temperature than that of *R*, and hence must reject *n* foot-pounds to a body at this temperature; that is to say, when the temperatures of *S* and *R* are fixed and also the quantity of heat to be absorbed, these determine the quantity which must be rejected.

Let the lines *ADF*, *BCE* (fig. 4) be the isothermals of a given fluid at temperatures equal to those of *R* and *S* respectively; and let *ABCD* represent a cycle in which *m* foot-pounds of heat are absorbed, and *n* foot-pounds rejected.

Let another cycle *DCEF* be now performed in which a similar quantity of heat is absorbed; therefore a similar quantity of heat must also be rejected, since the quantity of heat rejected is not dependent upon the nature of the fluid.

Thus, in the whole cycle *ABEF* we have a quantity of heat equal to $2m$ foot-pounds absorbed, and $2n$ foot-pounds rejected. And the same may be proved of any other multiple of *m* and *n*.

From this it is evident that if the temperature of the source of heat and of the refrigerator be fixed, the ratio of the quantities of heat absorbed and rejected in a reversible cycle is thereby determined irrespective of the nature of the fluid which performs the cycle.

18. **Absolute scale of temperatures.** Hitherto we have only spoken of temperatures as being either equal, or higher and lower, without considering by how much one temperature is higher than another. A scale is required by which to name degrees of temperature and thus to fix a standard of comparison for the temperatures of bodies which cannot be directly compared with one another.

Such a scale must of course be consistent with itself, but is otherwise quite arbitrary. Different scales have been proposed, and are in use, depending for the most part on the expansion which accompanies the increase of the sensible heat of some particular substance. It is desirable for scientific purposes to have a scale which shall be independent of the peculiarities of any single substance, and shall have a definite relation to some property common to all substances.

Of such scales the one which has been found by far the most advantageous depends upon the property of Carnot's Cycle, which we have just demonstrated. It is called the scale of absolute temperatures, and may be thus defined. *The numbers expressing degrees of absolute temperature are proportional to the quantities of heat absorbed and rejected at those temperatures in a reversible cycle.*

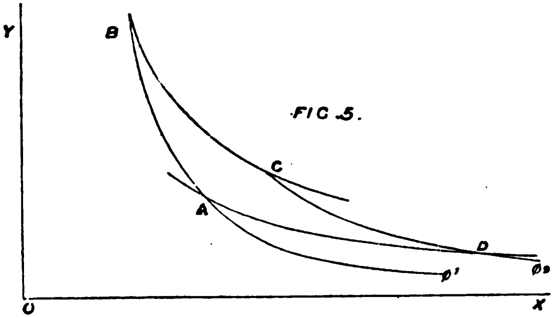


FIG. 5.

Let $BA\phi_1$ and $CD\phi_2$ be indefinitely produced adiabatic curves and AD, BC isothermals; then the numbers expressing on the absolute scale the temperatures of the fluid which correspond to the isothermal lines AD and BC, are proportional to the indefinitely prolonged areas $\phi_1 AD\phi_2$ and $\phi_1 BC\phi_2$. Let these numbers be denoted by τ_1 and τ_2, therefore

$$\frac{\tau_1}{\tau_2} = \frac{\text{area } \phi_1 AD\phi_2}{\text{area } \phi_1 BC\phi_2}.$$

From this it follows that

$$\frac{\tau_2 - \tau_1}{\tau_2} = \frac{\text{area } \phi_1 BC\phi_2 - \phi_1 AD\phi_2}{\text{area } \phi_1 BC\phi_2} = \frac{\text{area } ABCD}{\text{area } \phi_1 BC\phi_2}.$$

So that we may put the definition of absolute temperatures into the following form, which is very often useful:

The difference of the absolute temperatures of receiving and rejecting heat in Carnot's cycle is to the temperature at which heat is received, as the work done in the cycle is to the whole heat received.

The essential part of the absolute scale is the *ratio* of the numbers expressing degrees of temperature, the numbers themselves, or, what is the same thing, the size of the degrees may be fixed arbitrarily. For convenience this is so determined that between two standard temperatures there shall be the same number of degrees on the absolute scale as on the scales in ordinary use. The standard temperatures fixed upon are those of melting ice and of water boiling under a pressure of 29·922 ins. of mercury, which is the average atmospheric pressure. On Fahrenheit's scale there are 180 degrees in this interval, on the centigrade scale 100 degrees.

19. Absolute zero of temperature. Since the ratios of the numbers expressing degrees of absolute temperature are fixed, therefore the scale must have a fixed zero point which will be denoted by $\tau = 0$, whatever be the actual numbers used to express other temperatures. As we approach the value $\tau = 0$, that is to say, as the quantities of heat rejected in a cycle become smaller, the isothermals approach nearer to the line OX, and at last sensibly coincide with it, so that the zero of the absolute scale corresponds to a temperature at which no substance would exercise any expansive power, or be capable of performing any work whatever in virtue of possessing heat. In other words, the temperature $\tau = 0$ corresponds to the absolute privation of heat.

Of course such a temperature could never be experienced, but we shall show later on how an estimate is made of the interval between this zero point and the temperatures with which we have to deal experimentally.

20. The Thermodynamic function. The property of a substance which remains constant throughout such changes as are represented by an isothermal line is the temperature. A scale has now been established according to which we may denote any difference of two temperatures by a definite numerical value.

In the same way that property of a substance which remains constant throughout the changes represented by an adiabatic curve is called the *Thermodynamic function.*

A scale is required according to which we may express differences of Thermodynamic function by definite numerical values, just as differences of temperature are expressed.

As in the measurement of temperatures, so here any arbitrary scale might be taken, but the only one which can be of use to us is determined as follows:

The difference between the numerical values of the thermodynamic functions corresponding to any two adiabatics is equal to the quotient of the number of foot-pounds of heat absorbed or rejected in passing according to any isothermal line from one of these adiabatics to the other, divided by the number denoting the degree of absolute temperature corresponding to that isothermal.

Let $BA\phi_1$, $CD\phi_2$ (fig. 5) be adiabatics, and let ϕ_1, ϕ_2 represent the numerical values of the thermodynamic functions to which they correspond. Also let AD, BC be isothermals corresponding to the temperatures τ_1 and τ_2.

Then by definition

$$(\phi_2 - \phi_1) = \frac{\text{area } \phi_1 AD\phi_2}{\tau_1} = \frac{\text{area } \phi_1 BC\phi_2}{\tau_2}.$$

Therefore the quantities of heat absorbed and rejected in the operations, BC and DA are equal to $\tau_2(\phi_2 - \phi_1)$ and $\tau_1(\phi_2 - \phi_1)$ respectively.

From this it follows that

$$\text{area } ABCD = (\tau_2 - \tau_1)(\phi_2 - \phi_1),$$

or, the work done in Carnot's Cycle is numerically equal to the product of the difference of the temperatures multiplied into the difference of the thermodynamic functions of the fluid during the operations.

CHAPTER III.

SPECIFIC HEAT AND EVAPORATION.

21. **Heat absorbed at constant volume.** Consider now the communication of heat to a substance while its volume is kept constant.

The only case with which we have to deal is that in which the substance tends to expand with heat, and since this tendency is restrained there must evidently be an increase of pressure. Thus, on the diagram of energy, the changes produced will be represented by a straight line parallel to OY, and whose length represents this increase of pressure.

Since there is no expansion therefore no external work is performed in the process, and the whole heat absorbed goes to increase the intrinsic energy of the substance, as is evident from a figure.

All known substances have their temperatures raised by absorbing heat at constant volume, such rise being denoted on the diagram of energy by the intersection of the line representing the changes produced, with successive isothermals corresponding to higher temperatures.

The numerical ratio of the quantity of heat absorbed by one pound of the substance, to the difference of temperature produced in the process, is called the *Specific Heat at constant volume* of the substance; and when the quantity of heat is expressed in foot-pounds, as has been done here, the ratio is called the *Dynamical* Specific Heat at constant volume. This latter is usually denoted by the symbol K_v.

Since the ratio is not constant for all states of a substance, it is necessary that the changes produced in the operation from which it is calculated in any particular case, should be so small that the ratio does not sensibly alter throughout them, and in giving the value of the specific heat, the state of the substance during these changes should be also given, if the statement is to be accurate.

22. **Heat absorbed at constant pressure.** Take next the case of a substance receiving heat at constant pressure.

This is the most usual condition under which the effects of heat are observed, since the changes of pressure necessary to modify sensibly its effects upon solids and most liquids would be very great; and it is found that even in gaseous fluids, those changes can be most accurately observed which take place at constant pressure.

On a diagram of energy such changes are of course represented by a straight line parallel to OX, whose length corresponds to the change of volume which takes place, and whose distance from OX represents the intensity of the constant pressure.

The external work done during the operation is equal to the product of the pressure into the increase of volume. If the volume decrease, work must have been done upon the substance during the change.

Most substances, and probably all, in passing through certain states, absorb heat at constant pressure without having their temperature raised, until a certain definite quantity of heat has been absorbed.

When heat does produce an alteration of temperature in a substance, the ratio of the quantity absorbed to the rise in temperature is called the *Specific Heat at constant pressure* of the substance, or when the quantity of heat is expressed in foot-pounds, the *Dynamical Specific Heat at constant pressure.* This is generally denoted by the symbol K_p.

The specific heat at constant pressure, like that at constant volume, varies in different states of a substance: hence the changes produced in the operation from which the specific heat is calculated, must be so small that the ratio is sensibly constant throughout.

When the *specific heat* of a solid or liquid is spoken of, the specific heat at constant pressure is to be understood, as it is not generally possible to observe or calculate the specific heat at constant volume, except in the case of gases.

23. **Joule's Equivalent.** Specific Heat is termed *Dynamical* when the quantity of heat considered is expressed in foot-pounds, because the older unit of measurement was not the foot-pound, but that amount of heat which, acting on a pound of water at or near its temperature of greatest density, will raise its temperature through one degree Fahrenheit.

This quantity of heat is still called the *British Thermal Unit*, and when expressed in foot-pounds, is numerically equal to the Dynamical Specific Heat of water at or about its greatest density, which is found to be at a temperature of 39·1 Fahrenheit. The British Thermal Unit is equivalent to 772 foot-pounds of heat.

Hence, if the Specific Heat of a substance, according to this unit, be given, the Dynamical Specific Heat is found by multiplying it by 772. This number is known as Joule's Equivalent, because it was first accurately determined by the experiments of Dr Joule.

24. **Dilatability.** When the temperature of a substance is raised by the absorption of heat at constant pressure, there is another relation to be considered, namely, the ratio of the change of volume of one pound of the substance to the rise of temperature. This is called the *Dilatability.*

Like the specific heat, the dilatability is not constant for all states of a substance, and therefore it must be calculated for any given state of the substance from changes which are so small that throughout them the ratio does not alter sensibly.

In any given state of a substance the dilatability is numerically equal to the ratio of the difference of thermodynamic function to the corresponding difference of pressure when the substance undergoes any very small change according to an isothermal line, but these ratios have opposite signs, the one being positive when the other is negative. This may be proved as follows.

Let figure 6 represent, on a large scale, a small portion of the diagram of energy. Let a pound of the substance be initially in the state *A*, and let its pressure and volume be equal to p and v respectively.

Also let $BA\phi$, $AD\tau$ be the adiabatic and isothermal through *A*, and let them correspond to the thermodynamic function ϕ and the temperature τ.

Let *AB* represent a very small compression of the substance without transfer of heat, during which the temperature undergoes the very small change from τ to τ', and *AD* represent a very small expansion at constant temperature, during which the thermodynamic function increases from ϕ to ϕ', and the pressure falls from p to p'.

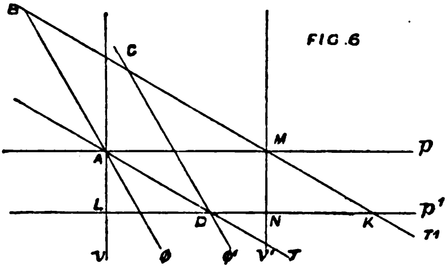


FIG. 6

Let $BC\tau'$ and $CD\phi'$ be the isothermal and adiabatic for the temperature τ', and thermodynamic function ϕ'.

The differences $(\tau' - \tau)$ and $(\phi' - \phi)$ are supposed to be so small that the isothermals and adiabatics of the figure are sensibly parallel straight lines throughout that part of their length which is under consideration.

Through *D* draw a straight line *KDL* corresponding to the constant pressure p' and cutting the isothermal for temperature τ' in *K*.

Through A draw AL a line of constant volume v to meet KDL in L, and AM a line of constant pressure p to meet $BC\tau'$ in M.

Through M draw MN a line of constant volume to meet KDL in N, and let the volume represented by it be v'.

Then AM is the increase of volume $(v' - v)$ which takes place during a rise of temperature $(\tau' - \tau)$ at constant pressure p.

Thus $\frac{v' - v}{\tau' - \tau}$ is the dilatability of the substance in the state A.

Also AL is the *fall* of pressure $(p - p')$ which accompanies an increase of thermodynamic function $(\phi' - \phi)$ at constant temperature τ.

Therefore $\frac{\phi' - \phi}{p - p'}$ or $-\frac{\phi' - \phi}{p' - p}$ is the ratio which is to be proved equal to the dilatability.

Now the parallelogram $ABCD$ is equal to the parallelogram $AMKD$ on the same base AD and between the same parallels AD, BK.

Again, this parallelogram $ADKM$ is equal to the rectangle $ALNM$ upon the same base AM and between the same parallels AM, LK.

Therefore the rectangle $ALNM$ is equal to the parallelogram $ABCD$.

But $ABCD$ represents one of Carnot's cycles, and its area is therefore equal to $(\tau' - \tau)(\phi' - \phi)$.

Therefore the rectangle $(AL)(AM) = (\tau' - \tau)(\phi' - \phi)$.

But $AL = p - p'$ and $AM = v' - v$.

Therefore $(p - p')(v' - v) = (\tau' - \tau)(\phi' - \phi)$, and therefore

$$\frac{v' - v}{\tau' - \tau}\ (p = \text{const.}) = -\frac{\phi' - \phi}{p' - p},\ (\tau = \text{const.}) \quad \text{Q.E.D.}$$

The geometrical proof of the proposition is taken from Professor Maxwell's *Theory of Heat*.

25. **Evaporation at constant pressure.** It has been mentioned that under certain conditions substances may absorb heat at constant pressure without having their temperatures raised in the process. This takes place during the change of the substance from the solid to the liquid state by fusion, or from the liquid to the gaseous state by evaporation. The latter is the process which is of importance in the present connexion.

Returning then to the pound of fluid contained in the cylinder as above described, suppose for the moment that it is all in the liquid state under a given pressure p.

If this pressure be maintained constant while heat is communicated, the temperature will continuously rise until it reaches a certain point, which is the highest that the particular fluid under consideration can attain at pressure p without passing into the gaseous state.

This is called the *Boiling Point* of the fluid at the given pressure.

Let the volume of the liquid be now equal to V_b, and let its state be represented by the point B on the diagram of energy (fig. 7).

If a farther quantity of heat be absorbed while the pressure still remains constant, a portion of the fluid must be converted from the liquid to the gaseous state, and as all known fluids expand in undergoing such a change, the total volume of the contents of the cylinder will thus be increased. At the same time there will be no alteration in the temperature of the fluid and, in fact, that part of it which is not evaporated will undergo no change whatever.

If yet more heat be absorbed the portion of the fluid which has been evaporated will remain unaltered, but a farther portion will be evaporated, and the process may be continued until at last the whole pound of fluid has been brought into the state of gas.

Let its volume then be equal to V_s, and its state be represented by the point S on the diagram.

A gaseous fluid while in the state which it assumes immediately on evaporation is known as *Saturated Vapour.*

When a fluid is undergoing evaporation or condensation it does not generally separate itself at once into two distinct parts, the one liquid and the other wholly gaseous; but small drops of liquid are held in suspension in the vapour for some time, causing the well-known cloudy appearance among vapours which are themselves transparent gases. These small drops tend to settle upon and damp the surface of any solid cooler than themselves with which they come in contact. To mark its freedom from any such admixture of liquid, a fluid in the state S is called *'Dry' Saturated Vapour.*

On the other hand, fluid which is passing through an intermediate state between B and S is sometimes spoken of as *Super-saturated Vapour;* not that the vapour itself is in any way different from dry saturated vapour, but to mark the fact that it carries with it small drops of liquid in suspension.

If after the fluid has arrived at the state S, it absorb any more heat at constant pressure, the whole mass will be capable of simultaneous alteration, and its temperature will rise in the usual manner.

The fluid is then called *Super-heated* in contradistinction to *'Saturated' vapour.*

26. **Latent Heat of Evaporation.** It was in the process of evaporation at constant pressure that it was first observed that heat might be absorbed by a substance without producing any rise of temperature; and as the nature of heat was not understood, the whole heat absorbed was supposed to lie hid in the vapour, no account being taken of the external work performed during the process, which is evidently equal to $(V_s - V_b)\,p$. Hence the name *Latent Heat of Evaporation* was applied to the whole amount of heat which disappears in the process of evaporation at constant pressure, and the name is still retained for convenience, although it would perhaps have been more accurate to have applied the name only to that part of the heat which actually remains hidden in the vapour, having been absorbed in performing internal work during the operation.

Taking the term however in its accepted sense, let L be the latent heat at pressure p of the pound of fluid, and let e be the quantity of heat which actually effects the evaporation by performing internal work. Then since the external work is equal to $(V_s - V_b)p$, and there is no increase of sensible heat; therefore

$$L = e + (V_s - V_b)\,p.$$

Putting $V_s - V_b = u$, so that u denotes the change of volume undergone by one pound of the fluid in the proccss of evaporation, we get

$$L = e + pu.$$

The quantity of heat represented by e will be referred to as the *Internal Heat of Evaporation.*

Since the process of evaporation is effected not by a simultaneous alteration of the whole mass of fluid, but by successive alteration of small portions, therefore it is evident that any portion xL of heat will evaporate a portion x of a pound of fluid and produce an alteration of volume, equal to xu cubic feet, and other effects in the same proportion.

27. **Relation of L to the pressure, temperature and volume.** A relation between the latent heat of evaporation and the pressure, temperature and change of volume of a fluid may be found as follows.

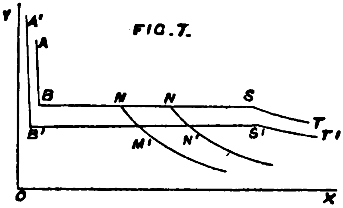


FIG. 7.

Let $ABST$ and $A'B'S'T'$ be two isothermals corresponding to the temperatures τ and τ' where the difference $(\tau - \tau')$ is very small.

Let the portions BS and $B'S'$ represent the changes undergone by the fluid during evaporation at the constant *pressures* p *and* p', then $p - p'$ will also be very small.

In BS take two points M and N representing the volumes v and v', where $(v'-v)$ is again very small, and through M and N draw adiabatics MM' and NN' cutting $B'S'$ in M' and N'.

Since the interval between these adiabatics, and the length of the portions MM', NN' with which we have to deal are very small, we may consider MM' and NN' as sensibly parallel straight lines. Therefore the area $MNN'M'$ is sensibly a parallelogram and its area equal to $(p-p')(v'-v)$. And this is equal to the work done in the cycle $MNN'M'$.

Also the heat absorbed in the expansion from M to N is proportional to the change of volume effected, and is equal to

$$\frac{MN}{BS}L=\frac{v'-v}{u}L.$$

But the work done in a reversible cycle between the temperatures τ and τ' is to the heat absorbed at temperature τ as $\tau-\tau'$ is to τ. Therefore

$$\frac{(p-p')(v'-v)}{\dfrac{v'-v}{u}L}=\frac{\tau-\tau'}{\tau},$$

therefore $$L=\tau\frac{p-p'}{\tau-\tau'}u\text{.....................}(1),$$

an equation which is true only when the quantities $p-p'$ and $\tau-\tau'$ are very small.

28. **Curve of Saturation.** Let a series of isothermals be drawn, as $A_1B_1S_1T_1$, $A_2B_2S_2T_2$, ... (fig. 8) of which the portions A_1B_1, A_2B_2,... represent the changes of pressure and volume of the fluid at constant temperature in the liquid state, B_1S_1, B_2S_2,... the process of evaporation, and S_1T_1, S_2T_2, ... the expansion of the super-heated vapour at constant temperature. A curve drawn through the points S_1, S_2,... will represent the changes which may be undergone by the fluid while it remains entirely in the state of saturated vapour. It is therefore known as the *Curve of Saturation.* The volume of all fluids in the state of saturated vapour decreases

as the pressure and temperature increase, and thus the curve of saturation slopes downwards from left to right, as shown in the figure.

On the other hand, the volume of every liquid at the boiling point increases with the pressure and temperature. Therefore a curve drawn through the series of points B_1, B_2,... will slope in the opposite direction to the curve of saturation, and the two will approach each other as the pressure increases, and at length meet. The physical interpretation of this is that at a certain temperature the liquid and gaseous states become continuous, there being no marked separation, such as that observed in the ordinary processes of evaporation and condensation, between them. This is called the *Critical Temperature* of the fluid. Above this temperature the fluid retains the properties of a gas under any pressure however great.

It is supposed that the permanent gases resist condensation into the liquid form, because the lowest temperatures which we are able to produce are still above their critical temperatures.

For certain substances the critical temperature has been accurately determined, for instance, that of carbonic acid is at 87·7° Fahr., and the corresponding pressure of saturation is about 74 atmospheres.

There are a few substances, however, which can readily be brought to the critical temperature. Water reaches it at about 773° Fahr. The corresponding pressure of saturation has not been yet determined; but both temperature and pressure are far higher than those met with in the practical applications of steam.

29. **Curves of constant weight of vapour.** When a pound of fluid, instead of being all in the state of liquid or of vapour, consists of a mixture in which there is a given weight of each, its changes may be represented by a *Curve of constant weight of vapour.*

Let x be the proportion of vapour; then the volume of the mixture is evidently equal to $xV_s + (1 - x)\ V_b$, and therefore to $V_b + x\,(V_s - V_b)$ or $V_b + xu$.

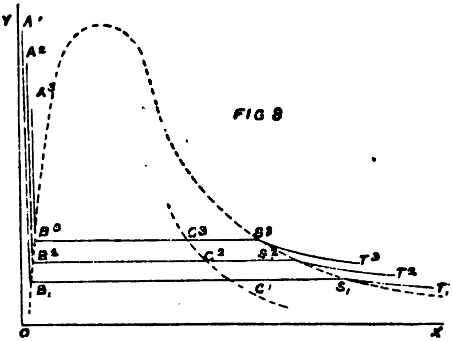


FIG 8

Hence if the form of the curves B_1B_2 ... and S_1S_2... be known, that of C_1C_2... the curve of constant weight x of vapour can at once be found by making

$$\frac{B_1C_1}{B_1S_1} = \frac{B_2C_2}{B_2S_2} = \ldots\ldots = x.$$

If these curves are considered as a series, the curves B_1B_2... and S_1S_2... may be looked on as the limits of the series when $x = 0$ and $x = 1$ respectively.

CHAPTER IV.

HYPERBOLIC AREAS.

30. **Hyperbolic areas.** In order that we may obtain our results without being dependent upon the methods of the Calculus, it is necessary to obtain a geometrical solution of a problem which is usually solved by integration.

We shall have frequent occasion to refer to it in our calculations, and may state it thus.

Problem.

Let OX, OY be two straight lines intersecting at right angles in O. Let AB be a curve such that the perpendicular distance of any point in it from the line OX is inversely proportional to the n^{th} power of the perpendicular distance of the same point from the line OY.

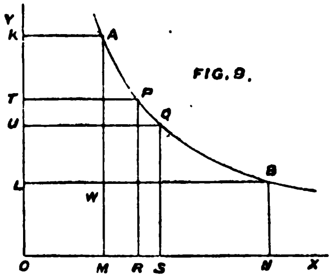


FIG. 9.

Let AM, BN be straight lines drawn perpendicular to OX.

It is required to find an expression for the area of the space included between the curve, the line OX, and any two lines such as AM, BN drawn perpendicular to OX.

Divide the straight line MN into any number m of equal parts; let RS be one of these parts, and through R and S draw RP, SQ parallel to OY to meet the curve in P and Q. Through A, P, Q, B draw AK, PT, QU, BL parallel to OX to cut OY in K, T, U and L, and let BL cut AM in the point W.

Put
$$AK = x_1, \qquad AM = y_1,$$
$$BL = x_2, \qquad BN = y_2,$$
$$\frac{ON}{OM} = \frac{x_2}{x_1} = r.$$

Also
$$PT = x, \qquad PR = y,$$
$$QU = x', \qquad QS = y'.$$

Since P is a point on the curve we have by supposition $y = \frac{c}{x^n}$, where c is a constant. Hence the rectangle $PT.TU$ or $x(y - y')$ is equal to $cx\left(\frac{1}{x^n} - \frac{1}{x'^n}\right)$.

In the same way the rectangle $QS.SR$ or

$$y'(x' - x) = \frac{c}{x'^n}(x' - x).$$

Dividing one by the other we get

$$\frac{PT.TU}{QS.SR} = \frac{x(y - y')}{y'(x' - x)} = \frac{x\left(\frac{1}{x^n} - \frac{1}{x'^n}\right)}{\frac{1}{x'^n}(x' - x)}$$

$$= \frac{x\,\frac{x'^n - x^n}{x'^n x^n}}{\frac{1}{x'^n}(x' - x)} = \frac{1}{x^{n-1}} \cdot \frac{x'^n - x^n}{x' - x} \text{ .... (1).}$$

Now $$x'^n = \{x + (x' - x)\}^n,$$
and this expanded according to the binomial theorem becomes

$$x'^n = x^n + nx^{n-1}(x' - x) + \frac{n(n-1)}{\lfloor 2} x^{n-2}(x' - x)^2 + \ldots\ldots$$

Substituting this value of x'^n in equation (1) we get

$$\frac{PT \,.\, TU}{QS \,.\, SR} = \frac{1}{x^{n-1}} \left\{ nx^{n-1} + \frac{n(n-1)}{\lfloor 2} x^{n-2}(x' - x) + \ldots \right\} \ldots\ldots (2).$$

By increasing m, the number of parts into which MN is divided, each of these parts can be made as small as we please, and may ultimately become less than any assigned limit. And when $(x' - x)$ becomes indefinitely small the higher powers, $(x' - x)^2$ and others, become indefinitely small in comparison with $(x' - x)$. Thus the series

$$nx^{n-1} + \frac{n(n-1)}{\lfloor 2} x^{n-2}(x' - x) + \ldots$$

may be made to differ from nx^{n-1} by a quantity less than any given limit, and is ultimately equal to nx^{n-1}.

Substituting this value for the series in equation (2) we have

$$\frac{PT \,.\, TU}{QS \,.\, SR} = n,$$

when SR and therefore TU are very small.

There are then a series of m rectangles of which $PT \,.\, TU$ is the type, and another series of m corresponding rectangles of which $QS \,.\, SR$ is the type, and each rectangle of the first series bears to the corresponding rectangle of the second series the ratio n to 1. Therefore the sum of the first series is equal to n times the second series of rectangles.

But as m is increased and SR diminished indefinitely, the area of the rectangle $QS \,.\, SR$ approaches to equality with the area $RPQS$ and may be made ultimately to differ from it by a quantity less than any given quantity, and the same is true of each of the other $m - 1$ rectangles of the series.

Therefore in the limit when m is indefinitely increased, the sum of the series of rectangles of which $QS \, . \, SR$ is the type, becomes equal to the area $MABN$.

And in the same way the sum of the series of rectangles of which $PT \, . \, TU$ is the type, may be shown to be ultimately equal to the area $KABL$.

Therefore $$\frac{\text{area } KABL}{\text{area} MABN} = n.$$

Therefore

$$\frac{\text{area } KABL - \text{area } MABN}{\text{area } MABN} = n - 1,$$

and

$$\text{area } MABN = \frac{1}{n-1}\,(\text{area } KABL - \text{area } MABN) \ldots (3),$$

but $$\text{area } KABL = x_1\,(y_1 - y_2) + \text{area } ABW,$$

and $$\text{area } MABN = y_2\,(x_2 - x_1) + \text{area } ABW.$$

Therefore, from equation (3),

$$\text{area } MABN = \frac{1}{n-1}\,\{x_1\,(y_1 - y_2) - y_2\,(x_2 - x_1)\},$$

or $$\text{area } MABN = \frac{x_1y_1 - x_2y_2}{n-1} \ldots\ldots\ldots\ldots\ldots\ldots (4),$$

or again,

$$\text{area } MABN = \frac{c}{n-1}\left(\frac{1}{x_1^{\,n-1}} - \frac{1}{x_2^{\,n-1}}\right) \ldots\ldots\ldots\ldots (5).$$

Equation (4) may be put in other forms by writing

$$\frac{x_2}{x_1} = r,$$

for instance,

$$\text{area } MABN = x_2y_2\left\{\frac{\frac{x_1y_1}{x_2y_2} - 1}{n-1}\right\} = x_2y_2 \, . \, \frac{r^{n-1} - 1}{n-1} \ldots\ldots (6).$$

3 –2

The results of equations (4) and (5) are perfectly general, and true whatever may be the value of n, but when n is put equal to unity the expressions take the indeterminate form $\frac{0}{0}$, and must be put into another shape to be of any use.

In order to effect this put $r^{n-1} = \{1 + (r-1)\}^{n-1}$, and expand according to the binomial theorem; therefore

$$r^{n-1} = 1 + (n-1)(r-1) + \frac{(n-1)(n-2)}{\underline{|2}}(r-1)^2 + \frac{(n-1)(n-2)(n-3)}{\underline{|3}}(r-1)^3 + \ldots\ldots$$

Substituting this value in equation (6),

$$\text{area } MABN = x_2y_2\left\{(r-1) + \frac{n-2}{2}(r-1)^2 + \frac{(n-2)(n-3)}{\underline{|3}}(r-1)^3 + \ldots\ldots\right\},$$

which is true whatever be the value of n.

Therefore putting $n = 1$ in this equation,

$$\text{area } MABN = x_2y_2\left\{(r-1) - \frac{(r-1)^2}{2} + \frac{(r-1)^3}{3} - \frac{(r-1)^4}{4} + \ldots\right\},$$

where the series is the well-known one for the Naperian logarithm of r. (See *Appendix.*)

Therefore area $MABN = x_2y_2 \log_e r$, when $n = 1$. But by hypothesis the curve AB is such that for every point in it $y = \frac{c}{x^n}$.

Hence $xy = c = x_2y_2$, when $n = 1$.

And therefore

$$\text{area } MABN = c \log_e r \ldots\ldots\ldots\ldots\ldots\ldots\ldots (7).$$

And thus the required expression has been found for the area in all cases. Q.E.F.

31. Small quantities of the form $\frac{x'-x}{x^n}$.

COROLLARY. It has been shown in the course of the foregoing solution that the area *MABN* is equal to the sum of the series of indefinitely small parallelograms of which *QS* . *SR* is the type, and which lie between the limits *OM* and *ON*. This series is ultimately equal to the series of small parallelograms of which *PR* . *RS* is the type.

Now the value of *QS* . *SR* is $y'(x'-x)$ or $c.\frac{x'-x}{x'^n}$; and the value of *PR* . *RS* is $y(x'-x)$ or $c.\frac{x'-x}{x^n}$.

The limits *OM* and *ON* are equal to x_1 and x_2 respectively, and the area *MABN* is equal to

$$\frac{c}{n-1}\left(\frac{1}{x_1^{n-1}}-\frac{1}{x_2^{n-1}}\right), \text{ by equation (5)};$$

or if $n=1$, then

$$\text{area } MABN = c\log_e\frac{x_2}{x_1}, \text{ by equation (7)}.$$

Therefore, in all cases, the sum of the whole series of indefinitely small quantities of the form $\frac{x'-x}{x^n}$ or $\frac{x'-x}{x'^n}$, which are included between the limits $x=x_1$ and $x=x_2$, is equal to

$$\frac{1}{n-1}\left(\frac{1}{x_1^{n-1}}-\frac{1}{x_2^{n-1}}\right),$$

or if $n=1$, the same series becomes equal to $\log_e\frac{x_2}{x_1}$.

Of course the successive terms of the series must be of the forms

$$\frac{x''-x'}{x'^n}+\frac{x'-x}{x^n}+\dots,$$

or else
$$\frac{x''-x'}{x''^n}+\frac{x'-x}{x'^n}+\ldots.$$

We have supposed, for convenience, that the successive quantities $(x''-x')$, $(x'-x)$,... are all equal, but this is not necessary. In order that the sum of the series may have the above values it is sufficient that the quantities $(x''-x')$, $(x'-x)$,... be each indefinitely small, and that their sum be equal to x_2-x_1.

CHAPTER V.

A PERFECT GAS.

32. **Hypothesis of a Perfect Gas.** We have now considered the most important of the thermal relations which hold universally for all fluids when they are either partly or wholly in the gaseous state.

In order to obtain special results from these general relations, it will be necessary to have some more particular knowledge of the properties of the substances dealt with, than is included in the general definition of a liquid or gaseous fluid.

As the simplest case we take first the calculation of the thermal relations of an hypothetical substance which is spoken of as a *Perfect Gas.*

The hypothesis may be stated thus.

In any given volume of a perfect gas, the pressure, the sensible heat and the internal work bear constant ratios to the whole quantity of heat which the gas possesses, that is to say, are proportional to its intrinsic energy, and are independent of the weight of gas which may be present in the given space.

If the gas contained in any given volume, have $(h+k)$ foot-pounds of heat of which k foot-pounds are sensible heat, and have in consequence a pressure p, then the gas contained in n equal volumes at equal pressure p must have $n(h+k)$ foot-pounds of heat of which nk foot-pounds are sensible heat. Therefore the intrinsic energy and sensible heat of any quantity of a perfect gas are proportional to the volume it *occupies when the* pressure is constant.

But this energy and sensible heat are, by hypothesis, proportional to the pressure when the volume is constant.

Therefore, in general, the intrinsic energy and sensible heat possessed by any quantity of a perfect gas are proportional to the product of the volume it occupies multiplied into its pressure.

33. **Relations of the Adiabatic Curves.** Let A and B represent two states of the gas at equal volume, and at pressures p and np respectively. Let BAK be the line of constant volume cutting OX in K, and let $AC\phi$ be the adiabatic through the point A.

Through B draw a curve $BD\phi'$ such that if any line DCL be drawn parallel to OY cutting the curve $BD\phi'$ in D, the adiabatic $AC\phi$ in C, and the line OX in L, then

$$\frac{DL}{CL}=\frac{BK}{AK}=n.$$

Therefore the indefinitely prolonged area $XKB\phi'$ is to the area $XKA\phi$ as BK to AK.

Hence the area $XKB\phi'$ represents the intrinsic energy of the gas in the state B. Therefore in expanding according to the curve $BD\phi'$, the gas must on the whole absorb as much heat as it rejects. Suppose then that in expanding to a given state D it absorb a certain quantity of heat, it follows that in expanding according to the curve $D\phi'$ it must reject an equal quantity of heat. But this is impossible, for the area $XLD\phi'$ is to the area $XLC\phi$ as LD to LC, and *therefore the area* $XLD\phi'$ is equal to the intrinsic energy

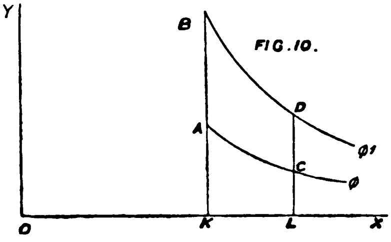


FIG. 10.

of the gas in the state D. Therefore at no part of the curve can the gas either absorb or reject heat, in other words, $BD\phi'$ is the adiabatic through the point B.

Hence if any two adiabatics be drawn, and also lines of constant volume as KAB and LCD cutting them in A, B and C, D, and the line OX in K and L, then

$$\frac{CL}{AK} = \frac{DL}{BK},$$

and therefore

$$\frac{AK - CL}{AK} = \frac{BK - DL}{BK}.$$

Or, when a perfect gas is expanded from one given volume to another according to an adiabatic curve, the fall of pressure is proportional to the initial pressure.

Again, let A and B represent two states of the gas in which the pressure is p_1 and the volumes v_1 and nv_1 respectively.

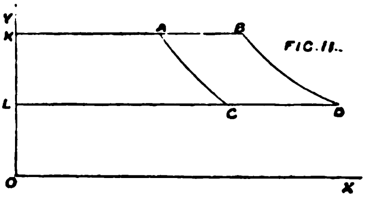


FIG. 11.

Let BAK be the line of constant pressure p_1, and let AC be the adiabatic through the point A. When the gas is expanded to the state C, let the pressure and volume be p_2, v_2.

The gas in the state B may be considered as consisting of n volumes each equal to v_1, and since, by hypothesis, the actual weight of gas in each equal volume does not affect the pressure and intrinsic energy, therefore each of these n volumes may be considered to contain $\frac{1}{n}$th of the quantity of gas whose state is represented at A, and yet the expansion of each, according to the adiabatic curve, will be exactly the same as that represented by AC. Thus, when the gas has been expanded till the pressure has fallen to p_2, each of the n volumes will have increased to v_2. Therefore, if BD be the adiabatic through B, and DCL the line of constant pressure through C cutting BD in D, we shall have

$$\frac{DL}{CL} = n = \frac{BK}{AK},$$

therefore also

$$\frac{CL}{AK} = \frac{DL}{BK},$$

and therefore

$$\frac{CL - AK}{AK} = \frac{DL - BK}{BK}.$$

That is to say, when the gas is expanded according to an adiabatic curve from one given pressure to another, the increase of volume is proportional to the initial volume.

Thirdly, let A and a represent any two states of the gas for which the pressures and volumes are P, V, and p, v, respectively. Let $A\phi_1$ and $a\phi_2$ be adiabatics, and let B be any point on the adiabatic $A\phi_1$.

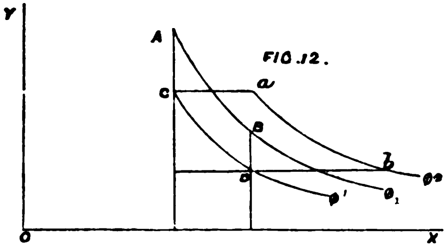


FIG. 12.

If the pressure and volume in the state B be mP, nV, we shall prove that on the adiabatic $a\phi_2$ a point may be found for which the pressure and volume are mp and nv.

Let C be the intersection of the line of constant volume through A with the line of constant pressure through a.

Therefore the pressure and volume in the state C are p, V.

Through C draw the adiabatic $C\phi'$, and through B draw BD parallel to OY to cut $C\phi'$ in D. Also through D draw Db parallel to OX to cut $a\phi_2$ in b.

Then the volume at the point D is equal to the volume at the point B, namely nV.

And since AB and CD are adiabatics and that the pressures at A, B and C are P, mP and p respectively; therefore the pressure at the point D is equal to mp.

Again, the pressure at the point b is also mp, and because CD and ab are adiabatics and that the volumes at the points C, D and a are V, nV and v, respectively; therefore the volume at the point b is nv.

Thus a point b has been found on the adiabatic through a for which the pressure and volume are mp and nv. Q.E.F.

COROLLARY. Now whatever be the ratio of the initial intrinsic energies in the two expansions AB and ab, the final intrinsic energies will have the same ratio; since

$$\frac{PV}{pv} = \frac{mP \,.\, nV}{mp \,.\, nv}.$$

It follows that if the intrinsic energies of the gas in any two states be equal, and if in expanding from these two states according to the adiabatic curves the gas perform equal quantities of work, so that the intrinsic energies at the end of the expansion are again equal, then the fall of pressure during these two expansions will be proportional to the initial pressures and the increase of volume proportional to the initial volumes.

34. Isothermal Lines. Equal quantities of sensible heat are those which produce equal temperatures in equal weights of any particular substance. But, by Art. 32, the sensible heat of a perfect gas is constant when its intrinsic energy is constant. Therefore if a given weight of a perfect gas undergo any series of changes in which the product of its pressure and volume does not vary, the temperature will remain constant. That is to say, the isothermal lines of a perfect gas are curves for which $pv =$ constant.

Such a curve is known in geometry as a rectangular hyperbola, and the lines OX, OY on the diagram of energy are its asymptotes.

Let AB be part of an isothermal line, and let the pressures and volumes of the gas in the states A and B be p_1, v_1 and p_2, v_2. Thus for any point on the curve

$$pv = p_1v_1 = p_2v_2.$$

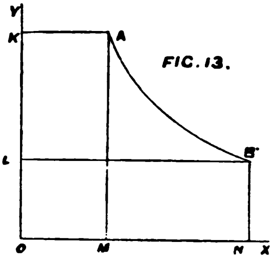


FIG. 13.

Draw AK, BL parallel to OX to meet OY in K, L and draw AM, BN parallel to OY to meet OX in M, N.

Then we have shewn above that

$$\text{area } MABN = p_1v_1 (\log_e v_2 - \log_e v_1)$$

$$= p_1v_1 \log_e \frac{v_2}{v_1} = p_1v_1 \log_e \frac{p_1}{p_2},$$

and area $MABN$ is equal to the work done by the gas in the expansion from A to B according to the isothermal line.

It is evident also that in the same way

$$\text{area } KABL = p_1v_1 (\log_e p_1 - \log_e p_2)$$

$$= p_1v_1 \log_e \frac{p_1}{p_2} = \text{area } MABN.$$

Again, since in the expansion AB the gas performs the work $MABN$, and that nevertheless its intrinsic energy is *unaltered:*

Therefore the heat absorbed during the expansion must be equal to the work done.

Let ϕ_1, ϕ_2 be the thermodynamic functions at *A* and *B*, and τ the temperature corresponding to the isothermal *AB*.

Therefore the heat absorbed in the expansion is $\tau(\phi_2 - \phi_1)$. Therefore

$$\tau(\phi_2 - \phi_1) = p_1 v_1 \log_e \frac{v_2}{v_1} = p_1 v_1 \log_e \frac{p_1}{p_2} \ldots\ldots\ldots\ldots (1).$$

35. Absolute Temperature. Equal quantities of sensible heat acting upon equal masses of any given substance produce, as we have said, equal temperatures; but since our scale of temperature is arbitrary, it still remains to be proved that it is so constructed that proportionate quantities of sensible heat acting on equal masses of a perfect gas produce proportionate temperatures, that is to say, temperatures denoted by numbers having the same proportion as the quantities of sensible heat; this we proceed to do.

Let *AB*, *CD* be isothermals corresponding to the temperatures τ and τ', and let *AC*, *BD* be adiabatics for which the thermodynamic functions are ϕ_1 and ϕ_2.

Let the pressures and volumes for the points *A*, *B* and *C* be p_1, v_1; p_2, v_2, and mp_1, nv_1. Because *AB* and *CD* are isothermals, therefore the intrinsic energy of the gas in the state *A* is equal to that in the state *B*, and again the

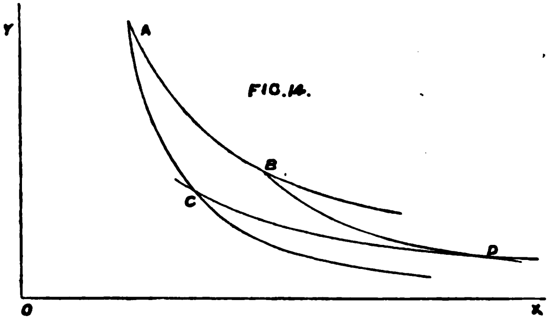


FIG. 14.

intrinsic energy in the state C is equal to that in the state D.

Therefore, if the gas be expanded according to the adiabatic curve AC, and again according to the curve BD, the fall of pressure and increase of volume in the two expansions will be proportional to the initial pressures and volumes respectively.

Therefore the pressure and volume for the point D are mp_2, nv_2.

Now $p_1v_1 \log_e \frac{v_2}{v_1}$ is the work done in expanding from A to B according to the isothermal AB, and the heat absorbed in the expansion is $\tau\,(\phi_2-\phi_1)$.

Therefore

$$p_1v_1 \log_e \frac{v_2}{v_1} = \tau\,(\phi_2 - \phi_1).$$

In the same way from the expansion CD we get

$$mp_1 \,.\, nv_1 \log_e \frac{nv_2}{nv_1} = \tau'\,(\phi_2 - \phi_1),$$

or

$$mp_1 \,.\, nv_1 \log_e \frac{v_2}{v_1} = \tau'\,(\phi_2 - \phi_1).$$

Therefore

$$\frac{\tau}{\tau'} = \frac{p_1v_1}{mp_1 \,.\, nv_1} = \frac{p_2v_2}{mp_2 \,.\, nv_2},$$

or the numbers expressing the temperatures of a perfect gas are proportional to the products of the pressures and volumes of the gas at these temperatures.

But the quantity of sensible heat in the gas is also proportional to the product of the pressure and volume.

Therefore different quantities of sensible heat acting on a given quantity of a perfect gas produce proportionate absolute temperatures.

Since temperatures are proportional to the products of *the pressures and* volumes in a perfect gas, therefore if

p_0, v_0, τ_0 be the pressure, volume, and temperature in any given state which may be taken as a standard, then in all other states of the gas

$$\frac{pv}{\tau} = \frac{p_0 v_0}{\tau_0}.$$

This is the fundamental equation of perfect gases, and indeed they are often defined as being substances for which such an equation holds good; the only other essential character of a perfect gas being that its Specific Heat is constant. This we proceed to prove.

36. **Specific Heat.** The Specific Heat of any substance at constant volume, is the ratio of the change of its intrinsic energy to the change of temperature at constant volume (see § 21, p. 21). But in a perfect gas the intrinsic energy bears a constant proportion to the temperature. Therefore the Specific Heat at constant volume is constant.

To find the relation between the specific heats at constant volume and at constant pressure; let A and B be two points on a line of constant pressure p_1, for which the volumes and temperatures are v_1, τ_1 and v_2, τ_2.

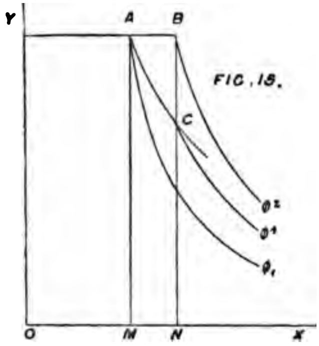


FIG. 15.

Through A and B draw AM, BN parallel to OY to meet OX in M and N.

Through A draw the isothermal AC cutting BN in C, and through A, B and C draw the adiabatics $A\phi_1$, $B\phi_2$, $C\phi'$.

Let the specific heat at constant volume be denoted by K_v, and the specific heat at constant pressure by K_p.

Therefore

$$K_v = \frac{\text{area } \phi' CB\phi_2}{\tau_2 - \tau_1}, \text{ or } K_v(\tau_2 - \tau_1) = \text{area } \phi' CB\phi_2.$$

In the same way

$$K_p = \frac{\text{area } \phi_1 AB\phi_2}{\tau_2 - \tau_1}, \text{ or } K_p(\tau_2 - \tau_1) = \text{area } \phi_1 AB\phi_2.$$

But the area $\phi_1 AB\phi_2$ is equal to the sum of the three areas $\phi_1 AC\phi'$, ABC and $\phi' CB\phi_2$, and of these the area $\phi_1 AC\phi'$ is equal to the area $MACN$, since one represents the heat received and the other the work done in the expansion AC. To each of these add the area ABC.

Therefore area $\phi_1 AC\phi'$ + area ABC = rectangle $MABN$.

Therefore area $\phi_1 AB\phi_2$ = rectangle $MABN$ + area $\phi' CB\phi_2$, and therefore

$$K_p(\tau_2 - \tau_1) = p_1(v_2 - v_1) + K_v(\tau_2 - \tau_1) \dots\dots\dots\dots (1),$$

but $$p_1 v_2 = \frac{p_0 v_0}{\tau_0}\tau_2, \text{ and } p_1 v_1 = \frac{p_0 v_0}{\tau_0}\tau_1,$$

so that $$p_1(v_2 - v_1) = \frac{p_0 v_0}{\tau_0}(\tau_2 - \tau_1).$$

Substituting this in equation (1) and dividing out by $(\tau_2 - \tau_1)$, we get

$$K_p = \frac{p_0 v_0}{\tau_0} + K_v \dots\dots\dots\dots\dots\dots\dots\dots (2).$$

Since $\frac{p_0 v_0}{\tau_0}$ is constant as well as K_v, this equation shows that K_p is also constant. Q.E.D.

We may put (2) in the form

$$\frac{p_0 v_0}{\tau_0} = K_p - K_v \dots\dots\dots\dots\dots\dots\dots\dots (3);$$

or, if we denote the ratio $\frac{K_p}{K_v}$ by the symbol γ we may write for equation (3)

$$\frac{p_0 v_0}{\tau_0} = K_v (\gamma - 1) \quad \text{....................} (4).$$

37. Differences of Thermodynamic Function. Let A and B be two points on a line of constant volume for which the pressures, temperatures, and thermodynamic functions are p_1, τ_1, ϕ_1, and p_2, τ_2, ϕ_2, respectively.

Let the straight line AB be divided into any number n of equal parts of which PQ is one, and let the pressures, temperatures, and thermodynamic functions in the states P and Q be p, τ, ϕ and p', τ', ϕ'. Through A, P, Q and B draw the adiabatics $A\phi_1$, $P\phi$, $Q\phi'$ and $B\phi_2$, and through P draw the isothermal PR cutting the adiabatic $Q\phi'$ in R.

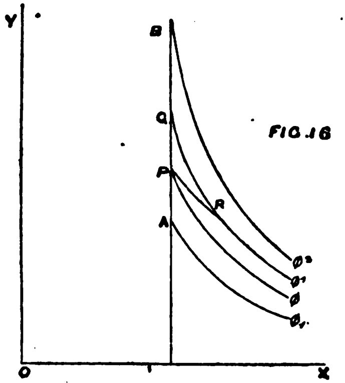


FIG. 16

The area $\qquad \phi PR\phi' = \tau (\phi' - \phi)$,

and area $\qquad \phi PQ\phi' = K_v (\tau' - \tau)$.

But if n, the number of parts into which AB is divided, be increased indefinitely, and thus each part such as PQ be indefinitely diminished, we may make the area $\phi PR\phi'$ as nearly as we please equal to the area $\phi PQ\phi'$, so that ultimately,

$$\tau(\phi'-\phi)=K_v(\tau'-\tau);$$

or,
$$\phi'-\phi=K_v\frac{\tau'-\tau}{\tau}\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1);$$

an equation which holds only when the differences $\phi'-\phi$ and $\tau'-\tau$ are very small.

In order to find the relation which holds between ϕ and τ when these differences are considerable we must take the sum of a number of such quantities.

Now the sum of all the n quantities of the form $(\phi'-\phi)$ between the limits ϕ_1 and ϕ_2 is evidently equal to $(\phi_2-\phi_1)$.

And by Art. 31, p. 37, the sum of the n quantities of the form $\frac{\tau'-\tau}{\tau}$ between the limits τ_1 and τ_2 is equal to $\log_e\frac{\tau_2}{\tau_1}$, or, since the pressure varies in proportion to the temperature, to $\log_e\frac{p_2}{p_1}$.

Therefore

$$(\phi_2-\phi_1)=K_v\log_e\frac{\tau_2}{\tau_1}=K_v\log_e\frac{p_2}{p_1}\ldots\ldots\ldots\ldots(1),$$

when the volume is constant.

Again, if in any two states of the gas the temperature τ is the same, while the pressures, volumes and thermodynamic functions are p_1, v_1, ϕ_1, and p_2, v_2, ϕ_2 respectively, we have by equation (1) of Art. 34, p. 45,

$$\tau(\phi_2-\phi_1)=p_1v_1\log_e\frac{v_2}{v_1}=p_1v_1\log_e\frac{p_1}{p_2}.$$

Therefore
$$(\phi_2-\phi_1)=\frac{p_1v_1}{\tau}\log_e\frac{v_2}{v_1},$$

but
$$\frac{p_1v_1}{\tau}=\frac{p_0v_0}{\tau_0}=K_p-K_v,\text{ by Art. 36.}$$

Therefore

$$(\phi_2-\phi_1)=(K_p-K_v)\log_e\frac{v_2}{v_1}=(K_p-K_v)\log_e\frac{p_1}{p_2}\ldots\ldots(2),$$

when the temperature is constant.

By combining equations (1) and (2) we can find the difference of the thermodynamic functions for any two states of the gas.

Let A and B represent any two states of the gas for which the pressures, volumes, temperatures and thermodynamic functions are p_1, v_1, τ_1, ϕ_1, and p_2, v_2, τ_2, ϕ_2.

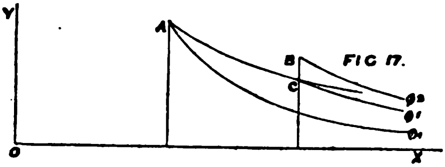


FIG 17.

Through the point A draw the isothermal AC, and through B draw BC parallel to OY cutting the isothermal AC in C.

Let ϕ' be the thermodynamic function for the point C, and through AB and C draw the adiabatics $A\phi_1$, $B\phi_2$, $C\phi'$.

Then since AC is an isothermal, therefore

$$\phi' - \phi_1 = (K_p - K_v) \log_e \frac{v_2}{v_1};$$

and since BC is a line of constant volume, therefore

$$\phi_2 - \phi' = K_v \log_e \frac{\tau_2}{\tau_1}.$$

Adding these two equations together, we get

$$\phi_2 - \phi_1 = K_v \log_e \frac{\tau_2}{\tau_1} + (K_p - K_v) \log_e \frac{v_2}{v_1} \dots\dots\dots \text{(3)},$$

which may also be written thus,

$$\phi_2 - \phi_1 = K_v \left\{\log_e \frac{\tau_2}{\tau_1} + (\gamma - 1) \log_e \frac{v_2}{v_1}\right\} \dots\dots\dots\dots \text{(4)}.$$

If the pressures at A and B are equal we have

$$\frac{v_2}{v_1} = \frac{\tau_2}{\tau_1},$$

and therefore (3) becomes

$$\phi_2 - \phi_1 = K_p \log_e \frac{\tau_2}{\tau_1} = K_p \log_e \frac{v_2}{v_1} \dots\dots\dots\dots \text{(5)},$$

when the pressure is constant.

4—2

Again, since

$$\frac{p_1 v_1}{\tau_1} = \frac{p_2 v_2}{\tau_2},$$

or

$$\frac{p_2 v_2}{p_1 v_1} = \frac{\tau_2}{\tau_1},$$

therefore

$$\log_\epsilon \frac{p_2}{p_1} + \log_\epsilon \frac{v_2}{v_1} = \log_\epsilon \frac{\tau_2}{\tau_1} \ldots\ldots\ldots\ldots\ldots (6),$$

or

$$\log_\epsilon \frac{v_2}{v_1} = \log_\epsilon \frac{\tau_2}{\tau_1} - \log_\epsilon \frac{p_2}{p_1} \ldots\ldots\ldots\ldots\ldots (7).$$

By substituting in equation (3) the value of $\log_\epsilon \frac{v_2}{v_1}$ taken from (7) we get the form

$$(\phi_2 - \phi_1) = K_p \log_\epsilon \frac{\tau_2}{\tau_1} - (K_p - K_v) \log_\epsilon \frac{p_2}{p_1} \ldots\ldots\ldots (8),$$

and by substituting in (3) the value of $\log_\epsilon \frac{\tau_2}{\tau_1}$ taken from (6) we find

$$(\phi_2 - \phi_1) = K_p \log_\epsilon \frac{v_2}{v_1} + K_v \log_\epsilon \frac{p_2}{p_1} \ldots\ldots\ldots (9),$$

or

$$(\phi_2 - \phi_1) = K_v \left(\gamma \log_\epsilon \frac{v_2}{v_1} + \log_\epsilon \frac{p_2}{p_1}\right) \ldots\ldots\ldots (10).$$

38. **Form of the Adiabatic Curve.** Since equation (10) of the last article is universally true, take for the lower limit a point for which $p_1 = 1$, $v_1 = 1$, and $\phi_1 = F$; and for p_2, v_2, ϕ_2 put p, v, ϕ, therefore

$$\frac{\phi - F}{K_v} = \gamma \log_\epsilon v + \log_\epsilon p,$$

or

$$pv^\gamma = \epsilon^{\left(\frac{\phi - F}{K_v}\right)} \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

is the equation between the pressure, the volume, and the thermodynamic function of a perfect gas.

It follows that for all points on any given adiabatic curve

$$pv = \text{constant} \ldots\ldots\ldots\ldots\ldots\ldots (12).$$

And therefore the work done in an expansion according to the adiabatic curve from pressure and volume p_1v_1 to p_2v_2 is equal to

$$\frac{p_1v_1 - p_2v_2}{\gamma - 1},$$

by equation (4), Art. 30.

Again, since $p_1v_1^\gamma = p_2v_2^\gamma$ by equation (12), therefore, by taking the logarithms of these,

$$\log\frac{p_2}{p_1} + \gamma\log\frac{v_2}{v_1} = 0 \text{ ....} (13).$$

But $\log\frac{p_2}{p_1} + \log\frac{v_2}{v_1} = \log\frac{\tau_2}{\tau_1}$ by equation (6); and subtracting this from equation (13),

$$(\gamma - 1)\log\frac{v_2}{v_1} = \log\frac{\tau_1}{\tau_2} \text{ ....} (14).$$

Also multiplying (13) by $\frac{\gamma - 1}{\gamma}$,

therefore $$(\gamma - 1)\log\frac{v_2}{v_1} = \frac{\gamma - 1}{\gamma}\log\frac{p_1}{p_2} \text{ ....} (15).$$

Therefore, taking (14) and (15) out of the logarithmic form, we have

$$\frac{\tau_1}{\tau_2} = \left(\frac{v_2}{v_1}\right)^{\gamma - 1} = \left(\frac{p_1}{p_2}\right)^{\frac{\gamma - 1}{\gamma}} \text{ ....} (16),$$

as the relations which hold between the pressures, volumes, and temperatures of any two points on the same adiabatic.

CHAPTER VI.

PERMANENT GASES AND THERMOMETRY.

39. Conditions of approximation to 'Perfect Gas.' No substance is known which corresponds exactly to the definition of a Perfect Gas; but all gaseous substances approximate to it more or less closely, and in general the more nearly as their pressures are diminished and their temperatures raised, that is to say, as they are removed farther from condensation into the liquid form.

Hence the name of a 'Perfect Gas.'

It has been mentioned that there are some gases which at ordinary pressures and temperatures are so far removed from the liquid state, that no combination of pressure and cold which has yet been applied to them has sufficed to condense them, and which are therefore known as permanent gases.

As might be expected, these are the substances which approach most nearly to the condition of perfect gases.

When a gaseous substance approaches condensation its difference from a perfect gas becomes well marked at ordinary pressures, but at very low pressures even saturated vapour follows the gaseous laws pretty closely, so that Rankine considers the vapour of water at 32° Fahr., although saturated, to be sensibly a perfect gas.

At this temperature the pressure of saturation is calculated to be about 12·3 lbs. on the square foot, or 0·085 lb. *on the square inch.*

40. **Properties of Air.** All the permanent gases follow very nearly the same thermal laws. We may take air as an example of the whole class of substances.

Let p_1v_1 be the product of the pressure and volume of air at some given temperature between 40° and 50° Fahr. and when $p_1 = 1$ atmosphere.

Then in a series of experiments at constant temperatures between these limits Regnault found that the values of the product pv at greater pressures stood thus:

$p =$ atmospheres	$\frac{p_1v_1}{pv}$	$\frac{pv}{p_1v_1}$
2	1·00122	0·9988
4	1·00352	0·9965
8	1·00683	0·9932
16	1·01004	0·9901

and when the temperature is higher the value of pv remains even more nearly equal to that of p_1v_1.

Thus for moderate differences of pressure the value of pv may be considered as sensibly constant.

If two vessels, one of which contains compressed air, while the other has had the air exhausted from it, have a communication opened between them, the air in expanding rapidly, so as to fill both vessels, will neither receive nor reject heat, nor, again, will it perform external work.

Therefore the intrinsic energy of the air will be the same at the end as at the beginning of the expansion.

But in making such experiments Dr Joule found that when the air had come to rest in the apparatus its temperature was almost exactly the same as it had been before the expansion, and therefore the product of the pressure and volume was also nearly the same.

Hence the intrinsic energy of air must remain very nearly constant during expansion according to an isothermal line.

Experiments also go to show that when air is expanded according to an adiabatic curve from one given volume to another the fall of pressure is nearly proportional to the initial pressure, and that when air is expanded in the same way from one given pressure to another, the increase of volume is proportional to the initial volume approximately.

Hence it may be shown, as in the case of a perfect gas, that for air $\frac{pv}{\tau}$ is nearly constant.

Similar results have been obtained with regard to the other permanent gases.

If τ_0 be taken to denote the absolute temperature of melting ice, and p_0v_0 be the product of the pressure and volume of a pound of air at that temperature, then it is found that

$$\frac{p_0v_0}{\tau_0} = 53{\cdot}21.$$

It is also found, as in the case of a perfect gas, that the specific heats of the permanent gases are sensibly constant. The value of the specific heat of air at constant pressure was found by M. Regnault from direct experiments to be 0·2379 of that of water at its temperature of greatest density. The specific heat of water has already been given as equal to 772 foot-pounds, therefore the dynamical specific heat of air at constant pressure is

$$K_p = 0{\cdot}2379 \times 772 = 183{\cdot}6.$$

But for a perfect gas by equation (2), Art. 36,

$$K_p = \frac{p_0v_0}{\tau_0} + K_v;$$

and thus for air $183{\cdot}6 = 53{\cdot}21 + K_v$ nearly.

Therefore $\qquad K_v = 130{\cdot}4,$

and $\qquad \frac{K_p}{K_v} = \gamma = 1{\cdot}408.$

The same results were obtained previously by Rankine, who took the value of γ from certain experiments on the velocity of sound in air, and deduced from it the specific heats of air by means of the equation $\frac{p_0 v_0}{\tau_0} = K_v(\gamma - 1)$ given at (4) in Art. 36, and thus found that

$$53{\cdot}21 = 0{\cdot}408\,K_v,$$

or $K_v = 130{\cdot}4$, as before.

41. The Air Thermometer. Suppose a glass tube of uniform bore closed at one end, to have a certain quantity of air confined in it by a drop of mercury which acts as a piston, so that allowing for the irregularities of the expansion of the glass itself under varying temperature, the distance of the mercury from the bottom of the tube is proportional to the volume of the included air.

This is called an Air Thermometer, and a scale of temperature such that on it equal temperatures are those which cause the mercury to move through equal spaces under constant pressure, is called the scale of the air thermometer. It is evidently very nearly the same as the absolute scale, and we shall show in the next article how the two may be compared.

If such an instrument be brought first to the temperature of melting ice, and then to that of water boiling under a pressure of 29·905 inches of mercury, which is the standard atmospheric pressure, the ratio of the distances of the drop of mercury from the bottom of the tube at the two temperatures will be as 1 : 1·3665.

Let the distance between the two readings of the thermometer at these temperatures be divided into 180 equal spaces; this being the number of degrees into which the same interval of temperature is divided according to Fahrenheit's scale; let the marking be continued in both directions till the whole tube is divided into lengths each equal to one of these 180 divisions, and let the marks be numbered successively beginning with zero at the bottom of the tube.

Then, if the pressure remain constant when the instrument is brought to any temperature, the reading will be the number denoting that temperature on the scale of the air thermometer.

Because the portion of the tube included between the marks for the freezing and the boiling point is equal to 0·3665 of the portion below the mark for the freezing point, and that the former portion contains 180 equal divisions, therefore the latter portion must contain $\frac{180}{0\cdot3665} = 491\cdot13$ of these divisions, that is to say, the number denoting the temperature of melting ice on the scale of the air thermometer is 491·13, and that denoting the boiling point of water is therefore 671·13. Also the zero of Fahrenheit's scale, which is 32 degrees of his thermometer below the freezing point, is about 459·13° on the air thermometer.

42. **Zero of absolute temperature and of the air thermometer.** At temperatures within the range of our experiments it has been found that the value of $\frac{pv}{\tau}$ is very nearly constant for air, and hence the scale of the air thermometer at these temperatures cannot be very different from the absolute scale.

In order however to complete the comparison it is important to find whether their zero points agree, and if not, to determine the difference between them, neither of which can of course be found by direct experiment.

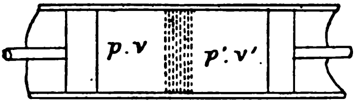
Joule and Thomson ascertained that there is a small difference, and determined its value by means of another and more accurate form of the experiment, which we have already mentioned in showing that the intrinsic energy of air at constant temperature is nearly constant.

The method may be explained as follows.

Suppose a cylinder to be fitted with two pistons one at each end, while the space between them is divided into two chambers by a porous plug.

At the commencement of the experiment let there be *a pound of air* on one side of the plug having pressure, volume, and intrinsic energy p, v and I while the piston is close to the plug on the other side. Now let the pressure on this piston be made equal to p', where p' is less than p, and thus let the air be forced through the plug, its volume and intrinsic energy per pound after passing through being v' and I'. When the whole pound of air has passed through the plug the work which has been done upon it by the piston acting with a pressure p through a space v will be pv, and thus the intrinsic energy of the air must have been increased by this amount. In the same way the work done by the air in forcing out the other piston with a pressure p' through a space v' must have diminished its intrinsic energy by the quantity $p'v'$.

FIG. 18.



Thus the result of the whole process is that

$$I' = I + pv - p'v',$$

or

$$I' + p'v' = I + pv \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1).$$

In a perfect gas, since the intrinsic energy is proportional to the product of the pressure and volume, while both are constant at constant temperature, this relation could only hold if the temperature of the gas were unaltered by passing through the plug, that is to say, the cooling effect due to the expansion without communication of heat would be exactly balanced by the heating effect of the work done during the expansion when this work is all expended in generating heat in the gas by means of the friction of its molecules.

All known gases however undergo a small change of temperature in the process: in hydrogen there is a slight rise of temperature. Air and all other known gases are somewhat cooled.

Let the absolute temperatures of the pound of air before and after passing the plug be τ and τ', and let these temperatures according to the scale of the air thermometer be denoted by t and t'.

The difference $\tau - \tau'$ is always very small, so that we may safely write

$$\tau - \tau' = t - t',$$

although the actual values of τ and τ' are not yet exactly known.

First, suppose the difference of pressures $p - p'$ to be very small.

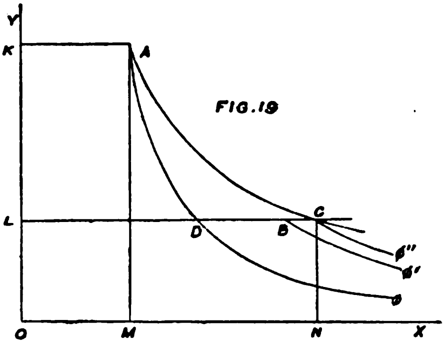


FIG. 19

Let the point A on the diagram of energy represent the state of the air before passing through the plug, and B its state afterwards.

Through A draw AC the isothermal for the absolute temperature τ, and through A and B draw AK, BL parallel to OX cutting OY in K and L, and AM, BN parallel to OY cutting OX in M and N.

Produce LB to cut AC in C, and let the volume for the point C be equal to v''.

Through A, B and C draw adiabatics $A\phi$, $B\phi'$ and $C\phi''$, and let $A\phi$ cut BL in D.

Since the change of pressure from the state A to the state B has been supposed very small, and since we know that the change of temperature is again very small in comparison with the change of pressure, therefore we may consider that the results do not differ appreciably from those of the change represented by the lines AC, CB, whatever *may be the real* process of expansion.

The heat absorbed by the gas in expanding according to the isothermal line from the state A to the state C would be $\tau(\phi''-\phi)$, which is represented by the area $\phi AC\phi''$; and the heat given out by the gas in changing from the state C to the state B at constant pressure would be $K_p(\tau-\tau')$, which is represented by the area $\phi' BC\phi''$.

Subtracting this from the area $\phi AC\phi''$ we see that the whole heat absorbed by the air in the processes AB, BC would be represented by the area ACD together with the area $\phi DB\phi'$, and be equal to $\tau(\phi''-\phi)-K_p(\tau-\tau')$.

But since $I'+p'v'=I+pv$ by (1), therefore area $XOLB\phi'$ = area $XOKA\phi$.

Subtracting from each the common area $XOLD\phi$ we have area $\phi DB\phi'$ = area $KADL$.

Add to each of these the area ACD.

Therefore the heat absorbed is represented by the area $KACL$.

Also since by supposition the change of volume from A to C is very small and the volume at B intermediate between the two we may write

$$\text{area } KACL=(p-p')v',$$

so that
$$\tau(\phi''-\phi)-K_p(\tau-\tau')=(p-p')v',$$

or
$$K_p(t-t')=\tau(\phi''-\phi)-(p-p')v' \quad \text{.........(2).}$$

It was shown in Chap. III. Art. 24, that the dilatability of a substance at constant pressure is numerically equal to the ratio which a small change of thermodynamic function bears to the accompanying small change of pressure at constant temperature, but is of opposite sign. In the present case this latter ratio is shown by the operation AC to be equal to $\frac{\phi-\phi''}{p-p'}$, and from the operation BC the dilatability is evidently equal to $\frac{v''-v'}{\tau-\tau'}$.

Hence
$$\frac{v''-v'}{\tau-\tau'}=\frac{\phi''-\phi}{p-p'},$$

and therefore $$\frac{v''-v'}{t-t'} = \frac{\phi''-\phi}{p-p'}.$$

Since the volume is proportional to the temperature when the pressure is constant, therefore this becomes

$$\frac{v'}{t'} = \frac{\phi''-\phi}{p-p'}, \text{ or } (\phi''-\phi) = (p-p')\frac{v'}{t'}.$$

Substituting this value of $(\phi''-\phi)$ in equation (2), therefore $$K_p(t-t') = \tau(p-p')\frac{v'}{t'} - (p-p')v',$$

or $$K_p(t-t') = \frac{v'}{t'}(p-p')\{\tau - t'\}\ldots,$$

But $\frac{v'p'}{t'} = \frac{v_0p_0}{t_0}$ very nearly, therefore we get

$$K_p(t-t') = \frac{v_0p_0}{t_0}\,\frac{p-p'}{p'}(\tau-t') \text{ ....(3)},$$

an equation which is true only when the change of pressure $p-p'$ undergone by the air in passing the plug is very small.

When the change of pressure is considerable the result must be found by summing up the results of a number of small changes, such as we have just investigated.

If in this case the initial and final pressures and temperatures be p_1, t_1 and p_2, t_2 it is found that t_1-t_2 is still very small when (p_1-p_2) is large.

Thus no appreciable error will be introduced if we consider τ and t' in the left-hand member of (3) to be constant quantities and to represent the same temperature, which is a mean between τ_1 and τ_2.

Also the sum of the whole number of small quantities of the form $\frac{p-p'}{p'}$ between the limits p_1 and p_2 is equal to $\log_e\frac{p_1}{p_2}$ by Art. 31.

Therefore we may write equation (3) in the form

$$K_p(t_1-t_2) = \frac{v_0p_0}{t_0}\log_e\frac{p_1}{p_2}(\tau-t').$$

Hence transposing and suppressing the accent on t' which is no longer necessary we get

$$\tau = t + \frac{K_p(t_1 - t_2)}{\frac{v_0 p_0}{t_0} \log_e \frac{p_1}{p_2}} \qquad \text{.....................(4)};$$

which shows that the zero of absolute temperature is rather lower than that of the air thermometer.

It was shown in Art. 41 that the zero of the air thermometer is 491·13° below the freezing point of water; experiments on the principle which has just been explained show that the zero of absolute temperature is 492·66° below the freezing point.

It should be noticed that when investigating the properties of thermal lines on the diagram of energy, we supposed the fluids under consideration to expand against or be compressed by external forces which at each instant differed infinitesimally from the expansive force of the fluids themselves.

The experiments described in Article 40 and in the present article deal with the action of a gas when the external pressure during some part of the experiment is much less than the expansive force of the gas. This process is termed the *free expansion* of gases.

The geometrical form of the calculations in this article is due to Professor Maxwell, and is taken from his work on the 'Theory of Heat.'

43. Thermometer filled with liquid. The reading of an air thermometer depends upon the external pressure as well as upon the temperature, and this makes its use in ordinary practice impossible.

On this account thermometers are generally used whose reading depends upon the expansion of some liquid, mostly mercury.

The tube of the thermometer is filled with liquid at a temperature higher than any at which it is afterwards to be used, and is then hermetically sealed.

When the thermometer cools there is a very nearly perfect vacuum in the tube above the surface of the liquid, and the readings of the instrument are independent of external pressure.

It is usual to have the tube enlarged at the bottom into a bulb so as to contain in a convenient compass a quantity of liquid which would fill a great length of tube if it were all of uniform bore.

All known liquids expand more rapidly at high temperatures than at lower ones; hence if a thermometer containing liquid be graduated at equal intervals, and made to correspond at 32° and 212° Fahr. with the air thermometer, the readings for intermediate temperatures would be somewhat below, and for all other temperatures above the readings of the air thermometer.

Regnault found that when the air thermometer marks 630° above the freezing point, the reading of the mercurial thermometer is 651·9° from the same point, showing a difference of 22°.

Not only does the liquid in a thermometer expand more rapidly as the temperature rises, but the glass tube itself does the same, and the two inequalities tend to neutralise one another, and make the divergence of the mercurial thermometer from the absolute scale smaller than it would otherwise be.

Hence for all practical purposes connected with heat-engines, as Rankine remarks, the mercurial thermometer made of common glass may be considered as coinciding sensibly with the absolute scale for temperatures not exceeding 500° Fahr.

For measuring low temperatures thermometers are sometimes filled with spirits of wine, but their scale differs more than that of the mercurial thermometer from the absolute scale of temperature.

CHAPTER VII.

STEAM.

44. Steam-gas. Steam, when moderately superheated, behaves very nearly as a permanent gas, and it approaches more closely to the perfectly gaseous state as it departs from the condition of saturated vapour, and as the pressure diminishes. At very low pressures even saturated vapour does not differ sensibly from a perfect gas.

The specific heat of steam-gas at constant pressure is 0·48 times that of water at its temperature of greatest density.

Thus the dynamical specific heat

$$K_p = 0{\cdot}48 \times 772 = 371.$$

Also if τ_0 denote the temperature of melting ice, at which temperature the saturated vapour of water is sensibly a perfect gas,

$$\frac{p_0 v_0}{\tau_0} = \frac{42141}{492{\cdot}66} = 85{\cdot}5\,;$$

the value of $p_0 v_0$ being calculated from the chemical composition of water.

Hence $$K_v = K_p - \frac{p_0 v_0}{\tau_0} = 285{\cdot}5,$$

and $$\gamma = \frac{K_p}{K_v} = 1{\cdot}3, \text{ very nearly.}$$

A result which is confirmed by other experiments.

Let p_1, v_1, ϕ_1 and p_2, v_2, ϕ_2 be the pressures, volumes, and thermodynamic functions of steam-gas in any two states; then, by equation (9) Art. 37,

$$(\phi_2 - \phi_1) = 371 \log_e \frac{v_2}{v_1} + 285{\cdot}5 \log_e \frac{p_2}{p_1}.$$

And again, if p_1, v_1, τ_1 and p_2, v_2, τ_2 be the pressures, volumes, and temperatures of steam-gas for any two points on the same adiabatic, we have by equation (16) Art. 38,

$$\frac{\tau_1}{\tau_2} = \left(\frac{v_2}{v_1}\right)^{0{\cdot}3} = \left(\frac{p_1}{p_2}\right)^{\frac{3}{13}}.$$

Thus the form of the adiabatic curve is given by the equation $pv^{1{\cdot}3}$ = constant; and the work done by one pound of steam in expanding according to such a curve from the state p_1v_1 to p_2v_2 is equal to

$$\frac{p_1v_1 - p_2v_2}{0{\cdot}3}.$$

The form of the isothermals for steam-gas is of course approximately a rectangular hyperbola, as in the case of the permanent gases.

45. Total heat of Gasification. The volume of water in the liquid state is so small as to be neglected in comparison with its volume in the state of perfectly gaseous steam, and therefore the isothermals for liquid water coincide sensibly with the line of no volume OY.

Again, the heat absorbed or given out by water in passing from one pressure to another according to an isothermal line may also be neglected; that is to say, the intrinsic energy of the liquid is sensibly constant at constant temperature.

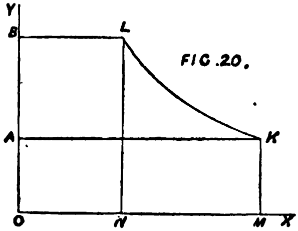


FIG. 20.

Let A and B represent two states of the liquid at any *given temperature* τ_0 but at different pressures.

Thus the intrinsic energy in the states A and B is sensibly the same.

In each case let the pressure be kept constant and heat supplied till the fluid has been brought to the perfectly gaseous form at the temperature τ, and let K, L now represent the states of the fluid.

Through K and L draw KM, LN parallel to OY to meet OX in M and N.

Therefore the rectangles $OAKM$ and $OBLN$ are equal, and represent the external work done by the fluid in the processes AK and BL respectively.

Also the intrinsic energies in the states K and L are equal, and we saw that the intrinsic energies in the initial states A and B were equal. Therefore the external work done, and the change of intrinsic energy produced in the two processes AK and BL are equal, and therefore also the heat absorbed in the process AK is equal to that absorbed in the process BL.

Therefore, in general, if water be raised from the liquid state at one given temperature to the perfectly gaseous state at another given temperature, the pressure being constant throughout the process, the heat absorbed is independent of the intensity of the constant pressure.

But at very low pressures the saturated vapour of water is sensibly a perfect gas, so that the heat absorbed in converting liquid water into the perfectly gaseous form at such pressures, is equal to the latent heat of evaporation.

Let τ_0 be the temperature of melting ice, and L_0 the latent heat of evaporation at this temperature.

Then the heat absorbed in converting liquid water at τ_0 into a sensibly perfect gas at the same temperature is equal to L_0. Also the heat absorbed in raising the gas so formed from the temperature τ_0 to the temperature τ at constant pressure is equal to $K_p(\tau-\tau_0)$. So that the whole heat absorbed in raising water from the liquid state at τ_0 to the perfectly gaseous state at τ is equal to $L_0+K_p(\tau-\tau_0)$, the pressure being constant during the process.

This quantity is conventionally named the "total heat of gasification."

The value of L_0 is found to be 842872, and we saw that $K_p = 371$, therefore

$$L_0 + K_p(\tau - \tau_0) = 842872 + 371\,(\tau - 492{\cdot}66)$$

is the total heat of gasification.

46. **Steam in other states than that of steam-gas.** The thermal properties of steam when mixed with water differ very considerably from those of a perfect gas, and at ordinary pressures the saturated vapour and even the slightly superheated vapour of water are found to be by no means perfectly gaseous.

No systematic investigation has yet been made of the thermal laws of steam in this last-named condition when it is in a state intermediate between that of saturated vapour and of perfect gas; but the behaviour of saturated steam both when dry and when mixed with liquid water has been most carefully observed, and the results formulated.

A simple hypothesis with regard to the nature of a perfect gas has been a sufficient basis on which to construct a connected series of thermal laws expressing very closely the results of actual experiments upon the various substances classed as nearly perfect gases.

No such basis has been found for the laws of saturated vapour and its mixture with liquid water; and we are therefore dependent on formulæ which simply condense the results of experiment without implying any connecting hypothesis and which are known as empirical formulæ. These being mostly constructed for temperatures measured by thermometers containing mercury and marked with the ordinary scales, it will often be convenient to use one of these scales here.

We shall use the letter T to denote temperatures measured according to Fahrenheit's scale, in which the temperature of melting ice is marked 32°, and the temperature of water boiling under standard atmospheric pressure is marked 212°.

Fahrenheit's scale is therefore connected with the absolute scale by the equation

$$T = \tau - 460{\cdot}66 \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1).$$

47. Specific heat of liquid water. Before examining the thermal laws of vapour it will be necessary to find the heat absorbed in raising liquid water from one given temperature to another.

The specific heat of most solids and liquids is not constant, but increases as the substance expands.

Thus the specific heat of liquid water is least at 39·1° Fahr., which is the temperature of greatest density.

As has been said before, Dr Joule determined its dynamical specific heat at this temperature to be 772.

The method employed in obtaining this result was, to expend a measured quantity of work entirely in producing heat by friction in a known weight of water, when the ratio of the work expended to the rise in temperature was found to be 772 foot-pounds of work per pound of water raised through one degree of temperature on Fahrenheit's scale. Experiments made by Regnault show that the specific heat at other temperatures is given by the formula

$$K = 772\,\{1 + 0{\cdot}000000309\,(T - 39{\cdot}1)^2\}\ldots\ldots\ldots(1),$$

or

$$K = 772 + 0{\cdot}000238548\,(T - 39{\cdot}1)^2\ldots\ldots\ldots\ldots(2).$$

That is to say, the heat necessary to raise one pound of liquid water through a very small interval of temperature $(T' - T)$ is equal to

$$772\,(T' - T) + 0{\cdot}000238548\,(T - 39{\cdot}1^\circ)^2\,(T' - T)\ldots\ldots(3).$$

For convenience we may write

$$T - 39{\cdot}1 = \theta, \text{ and } T' - 39{\cdot}1 = \theta'.$$

Therefore $T' - T = \theta' - \theta$, and (3) becomes

$$772\,(\theta' - \theta) + 0{\cdot}000238548\theta^2\,(\theta' - \theta)\ldots\ldots\ldots\ldots(4).$$

In order to find the quantity of heat necessary to raise one pound of water through a considerable interval of temperature from T_1 to T_2, it is necessary to add together all the series of small quantities of the form given in the expression (3) which are included between the limits of temperature T_1 and T_2, or, what is the same thing, all the series of small quantities of the form given in the expression (4) which are included between the limits θ_1 and θ_2.

Now the sum of all the small quantities $(\theta' - \theta)$ between these limits is evidently equal to $(\theta_2 - \theta_1)$, and the small quantity $\theta^2 (\theta' - \theta)$ may be written in the form $\dfrac{\theta' - \theta}{\theta^{-2}}$.

But by Art. 31, Chap. IV., the sum of all the small quantities of the form $\dfrac{\theta' - \theta}{\theta^n}$ included between the limits θ_1 and θ_2 is equal to

$$\frac{1}{n-1}\left(\frac{1}{\theta_1^{n-1}} - \frac{1}{\theta_2^{n-1}}\right);$$

and putting $n = -2$, this becomes

$$\frac{1}{3}(\theta_2^3 - \theta_1^3).$$

Writing for θ_1 and θ_2 their values, we get for the sum of all the small quantities of the form given in (3) between the limits T_1 and T_2.

$$772\,(T_2 - T_1) + \frac{1}{3} \times 0{\cdot}000238548\,\{(T_2 - 39{\cdot}1^\circ)^3 - (T_1 - 39{\cdot}1^\circ)^3\},$$

or $$772\,[(T_2 - T_1) + 0{\cdot}000000103\,\{(T_2 - 39{\cdot}1)^3 - (T_1 - 39{\cdot}1)^3\}].$$

The heat absorbed by one pound of liquid water in rising from the temperature of melting ice to the temperature T will be denoted by h.

Therefore by putting 32° for T_1 and T for T_2, we get

$$h = 772\,[(T - 32) + 0{\cdot}000000103\,\{(T - 39{\cdot}1)^3 + (7{\cdot}1)^3\}] \ldots (5).$$

48. **Total heat of evaporation.** The total heat of gasification has been defined as being the whole heat necessary to raise one pound of water from the liquid state at the temperature of melting ice to the perfectly gaseous state at any given temperature T, the pressure being constant during the operation.

It has been shown to be equal to

$$L_0 + K_p\,(T-32),$$

or

$$842872 + 371\,(T-32).$$

The heat necessary to raise one pound of water to the state of saturated vapour under the same conditions is called the *total heat of evaporation*, and will be denoted by H.

The value of H has been determined by the experiments of Regnault, and is expressed by an empirical formula of the same form as that for the total heat of gasification. According to this

$$H = 842872 + 235\,(T-32) \ldots\ldots\ldots\ldots(1).$$

49. **Latent heat of evaporation.** The process during which the total heat of evaporation H is absorbed, consists of two parts, namely, first the raising of the pound of water in the liquid state from 32° Fahr., the temperature of melting ice, to the given temperature T, and secondly the evaporation of this water at constant pressure and temperature from the state of liquid to that of saturated vapour.

By equation (5) Art 47, the quantity of heat absorbed in the first of these operations is

$$h = 772\,[(T-32) + 0{\cdot}000000103\,\{(T-39{\cdot}1^\circ)^3 + (7{\cdot}1)^3\}],$$

and the quantity of heat absorbed in the second operation is that which has been spoken of in Art. 26, Chap. III., as the latent heat of evaporation and denoted by L.

Hence we have

$$L = H - h \ldots\ldots\ldots\ldots\ldots\ldots(1),$$

therefore

$$L = 842872 + 235\,(T-32)$$
$$-\,772\,[(T-32) + 0{\cdot}000000103\,\{(T-39{\cdot}1)^3 + (7{\cdot}1)^3\}]\ldots(2),$$

or

$$L = 860056 - 537\,T - 0{\cdot}000079516\,\{(T-39{\cdot}1)^3 + (7{\cdot}1)^3\}\ldots(3).$$

Equation (3) expresses very accurately the results of experiment, but is rather complicated.

In dealing with steam-engines the range of temperatures of saturated steam generally met with is from about 100° Fahr.

to 350° Fahr., which corresponds to a range of pressures of saturation from about $\frac{1}{15}$th of an atmosphere to 9 atmospheres; and between these limits the latent heat of evaporation is expressed very nearly by the simpler formula

$$L = \alpha - \beta T \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4),$$

where $\alpha = 861250$ and $\beta = 546$.

It is sometimes convenient to have this in the form

$$L = \alpha' - \beta\tau \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5),$$

where $\alpha' = 1112770$, and $\beta = 546$ as before.

50. **Relation between pressure and temperature of saturation.** The pressures of saturation corresponding to various temperatures were determined by Regnault from a series of experiments, the results of which have been expressed in various empirical formulæ.

The form given by Rankine is

$$\log_{10} p = A - \frac{B}{\tau} - \frac{C}{\tau^2} \ldots\ldots\ldots\ldots\ldots\ldots (1),$$

which is simpler than that given by Regnault himself, and corresponds very accurately with the results of his experiments when

$A = 8{\cdot}28203$; $\log B = 3{\cdot}4414752$ and $\log C = 5{\cdot}5839751$.

These values are slightly different from those given by Rankine, because the absolute zero of temperature has here been taken at $-460{\cdot}66$. These constants substituted in equation (1) give the value of p in pounds on the square foot. If the value of p be required in pounds on the square inch, the first constant must be diminished by $\log_{10} 144$, and will then be equal to $6{\cdot}12367$ instead of $8{\cdot}28203$ as before. The other two constants remain unaltered.

From equation (1) it follows that the inverse formula giving the temperature in terms of the pressure of saturation is

$$\frac{1}{\tau} = \sqrt{\frac{A - \log_{10} p}{C} + \frac{B^2}{4C^2}} - \frac{B}{2C} \ldots\ldots\ldots\ldots (2),$$

where $\frac{B}{2C} = 0{\cdot}0036014$ and $\frac{B^2}{4C^2} = 0{\cdot}0000130$.

51. **Curves of Saturation and constant weight of vapour.** If the volumes of one pound of saturated vapour at different pressures and temperatures could be accurately determined by experiment, an empirical formula could be at once constructed which would give the form of the curve of saturation, but as this has not yet been found possible the volumes are determined indirectly, by means of formulæ already given.

Let p_1, p_2 be pressures of saturation corresponding to temperatures τ_1, τ_2; therefore from (1) of Art. 50,

$$\log_{10}p_2 - \log_{10}p_1 = \left(\frac{B}{\tau_1} - \frac{B}{\tau_2}\right) + \left(\frac{C}{\tau_1^2} - \frac{C}{\tau_2^2}\right);$$

therefore

$$\log_e \frac{p_2}{p_1} = \left\{B\left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right) + C\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right)\right\}\log_e 10 \ldots\ldots (1).$$

Now the sum of all the small quantities of the form $\frac{p-p'}{p}$ between the limits p_1 and p_2 is equal to $\log_e \frac{p_2}{p_1}$, by Art. 31.

If we put $p_1 = p'$ and $p_2 = p$, then the only small quantity of this form between the given limits is the one $\frac{p-p'}{p}$.

Therefore $\log_e \frac{p}{p'} = \frac{p-p'}{p}$ when $(p-p')$ is very small, so that we may write (1) in the form

$$\frac{p-p'}{p} = \left\{B\left(\frac{1}{\tau'} - \frac{1}{\tau}\right) + C\left(\frac{1}{\tau'^2} - \frac{1}{\tau^2}\right)\right\}\log_e 10 \ldots (2),$$

when $(p-p')$ and therefore also $(\tau - \tau')$ are very small.

But $\frac{1}{\tau'} - \frac{1}{\tau} = \frac{\tau - \tau'}{\tau\tau'}$, and by making $(\tau - \tau')$ small enough this may be made to differ as little as we please from $\frac{\tau - \tau'}{\tau^2}$.

Thus ultimately $\frac{1}{\tau'} - \frac{1}{\tau} = \frac{\tau - \tau'}{\tau^2}$.

In the same way

$$\frac{1}{\tau'^2}-\frac{1}{\tau^2}=\frac{\tau^2-\tau'^2}{\tau^2\tau'^2}=\frac{(\tau-\tau')(\tau+\tau')}{\tau^2\tau'^2}=\frac{2\tau(\tau-\tau')}{\tau^4}=\frac{2(\tau-\tau')}{\tau^3}$$

ultimately.

And substituting these values in (2)

$$\frac{p-p'}{p}=\left(\frac{B}{\tau^2}+\frac{2C}{\tau^3}\right)(\tau-\tau')\log_e 10,$$

or $$\tau\frac{p-p'}{\tau-\tau'}=2{\cdot}3026\left(\frac{B}{\tau}+\frac{2C}{\tau^2}\right)p \quad\ldots\ldots\ldots\ldots(3),$$

when $(p-p')$ and $(\tau-\tau')$ are very small.

But from equation (1) of Art. 27, Chap. III.,

$$u=\frac{L}{\tau\dfrac{p-p'}{\tau-\tau'}},$$

and from equation (4) of Art. 49,

$$L=\alpha'-\beta\tau.$$

Therefore $$u=\frac{\alpha'-\beta\tau}{2{\cdot}3026\left(\dfrac{B}{\tau}+\dfrac{2C}{\tau^2}\right)p}\quad\ldots\ldots\ldots\ldots\ldots\ldots(4).$$

Strictly speaking u is the difference between the volumes of water in the forms of liquid and of saturated vapour, but the former is so small that it may be neglected in comparison with the latter, and we may write approximately

$$v=\frac{\alpha'-\beta\tau}{2{\cdot}3026\left(\dfrac{B}{\tau}+\dfrac{2C}{\tau^2}\right)p}\quad\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

for the volume of one pound of saturated vapour at the temperature τ and pressure p. From this with the help of equation (1) Art. 50, which gives $\log_e p=A-\frac{B}{\tau}-\frac{C}{\tau_2}$, any number of points can be found on the curve of saturation for aqueous vapour.

Again, in the evaporation of a given weight x of a pound of water at constant pressure the change of volume produced is xu, and when x does not differ very greatly from unity the volume of liquid water will still be so small that it may be neglected in comparison with the volume of vapour, and thus for any point on the curve of constant weight of vapour x we may write

$$v = x \frac{\alpha' - \beta\tau}{2{\cdot}3026\left(\frac{B}{\tau} + \frac{2C}{\tau^2}\right)p} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (6).$$

The relations between pressure and volume involved in the above formulæ are very complicated, but by calculations of numerical results from these formulæ it has been found that the curve of saturation up to pressures of about 16 atmospheres corresponds very closely with the curve given by the equation

$$pv^n = \text{constant} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (7),$$

where $n = \frac{1}{0{\cdot}9393} = 1{\cdot}0646$, according to Zeuner, while Rankine uses the approximate value $n = \frac{17}{16}$.

Denoting by v the volume of one pound of saturated vapour, the curve of constant weight of vapour x is evidently

$$p\,(xv)^n = \text{constant} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (8),$$

when x is not very much less than unity. This also becomes pv^n = constant when v is put for the volume of the mixture of water and vapour under consideration.

52. **Areas bounded by the curve of saturation.** Let A and B be two points on the curve of saturation, and let the corresponding pressures, volumes and temperatures be p_1, v_1, τ_1 and p_2, v_2, τ_2 respectively.

Through A and B draw AK, BL parallel to OX and AM, BN parallel to OY.

Then since the form of the curve of saturation is given by the equation pv^n = constant, the area

$$MABN = \frac{p_1v_1 - p_2v_2}{n-1} = \frac{p_1v_1 - p_2v_2}{0{\cdot}0646},$$

since $$n = 1{\cdot}0646.$$

In the same way

$$\text{area } KABL = n \cdot \frac{p_1v_1 - p_2v_2}{n-1} = \frac{p_1v_1 - p_2v_2}{1 - \dfrac{1}{n}} = \frac{p_1v_1 - p_2v_2}{0\cdot0607}.$$

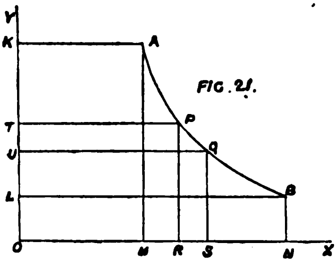


FIG. 21.

The value of this latter area can also be found in a simple form without assuming the equation $pv^n = \text{constant}$, as we proceed to show.

The comparison of the numerical values obtained by the two methods affords a test of the accuracy of this equation.

Let the straight line KL be divided into any number m of equal parts and let TU be one of these parts.

Through T and U draw TP, UQ parallel to OX to meet the curve of saturation in P and Q, and let the pressures, volumes and temperatures for the points P and Q be p, v, τ and p', v', τ'. When m is indefinitely increased and the distance TU therefore indefinitely diminished, we have ultimately area $TPQU = (p - p')\,v$.

By equation (1) Art. 27, Chap. III.,

$$L = \tau \frac{p - p'}{\tau - \tau'} u.$$

Therefore $$(p - p')\,u = \frac{\tau - \tau'}{\tau} L,$$

or, neglecting the volume of liquid water,

$$(p - p')\,v = \frac{\tau - \tau'}{\tau} L,$$

and by equation (4) Art. 49,

$$L = \alpha' - \beta\tau.$$

Therefore $(p - p')\,v = \alpha' . \frac{\tau - \tau'}{\tau} - \beta(\tau - \tau')$.........(1),
an equation which is true only when $p - p'$ and $\tau - \tau'$ are very small.

Adding together the whole of the series of m quantities such as $(p - p')\,v$ included between the limits $p_1 v_1$ and $p_2 v_2$, the sum is evidently equal to the whole area *KABL*.

Adding together the corresponding series of m quantities of the form $\alpha' \frac{\tau - \tau'}{\tau} - \beta(\tau - \tau')$ between the limits τ_1 and τ_2, we get for the sum of the small quantities such as $\alpha' \frac{\tau - \tau'}{\tau}$ the expression $\alpha' \log_e \frac{\tau_1}{\tau_2}$; while the sum of the small quantities such as $\beta(\tau - \tau')$ is equal to $\beta(\tau_1 - \tau_2)$.

Therefore from equation (1),

$$\text{area } KABL = \alpha' \log_e \frac{\tau_1}{\tau_2} - \beta(\tau_1 - \tau_2) \text{............}(2),$$

or putting for α' and β their numerical values from Art. 49,

$$\text{area } KABL = 1{,}112{,}770 \log_e \frac{\tau_1}{\tau_2} - 546(\tau_1 - \tau_2) \text{......}(3).$$

53. **Adiabatics of a mixture of water and saturated vapour.** In a mixture of a liquid with its saturated vapour the isothermals coincide with lines of constant pressure, so that the only important thermal lines whose form remains to be investigated are the adiabatics.

Let $AB\phi$ represent an adiabatic of a mixture of liquid water with aqueous vapour, and let the pressures, volumes and temperatures for the points A and B, be p, v, τ and p', v', τ' respectively.

Also let the weight of vapour in the mixture when in the states A and B be x and x'. Through A and B draw AM, BN parallel to OY to meet OX in M and N.

As in Art. 47, let h be the quantity of heat necessary to raise one pound of liquid water from the temperature of melting ice to the temperature τ.

Neglecting the small quantity of external work done by the expansion of the water during the process, the whole quantity of heat h may be considered as remaining in the liquid, and as an increase of intrinsic energy.

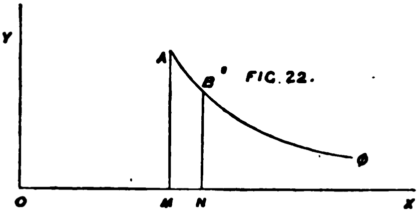


FIG. 22.

Again, as in Art. 26, let e be the internal heat of evaporation of one pound of water at temperature τ, then the internal heat of evaporation of a weight x of water will be xe.

Thus the total increase of the intrinsic energy of the fluid during the process of having its temperature raised from that of melting ice to τ, and then having a portion x evaporated at constant temperature τ, is $h + xe$.

In the same way when the pound of fluid undergoes a similar process in which the ultimate temperature is τ' and the weight of vapour x', the increase of intrinsic energy during the process may be denoted by $h' + x'e'$.

Thus the difference of the intrinsic energy of the fluid in the states A and B is

$$(h - h') + (xe - x'e').$$

And this difference is evidently equal to the area $MABN$.

Now suppose that the change of state from A to B is *very small, therefore* the area $MABN$ is sensibly equal to

$p'(v'-v)$, or, neglecting the change in the volume of liquid water produced by change of temperature,

$$\text{area } MABN = p'(x'u' - xu),$$

where u and u' are, as before, the differences between the volumes of liquid water and of saturated vapour at the temperatures τ and τ'.

But we saw that

$$\text{area } MABN = (h-h') + (xe - x'e').$$

Therefore

$$(h-h') + (xe - x'e') + p'(xu - x'u') = 0 \text{ ......(1)},$$

which by the addition and subtraction of xpu becomes

$$(h-h') + \{x(e+pu) - x'(e'+p'u')\} - x(p-p')u = 0\text{....(2)}.$$

But $e + pu = L$ the latent heat of evaporation at temperature τ, by Art. 26, and $e' + p'u' = L'$ the latent heat of evaporation at temperature τ'.

Therefore we may write (2) in the form

$$(h-h') + (xL - x'L') - x(p-p')u = 0 \text{ ......(3)}.$$

Now by equation (1) Art. 27, $L = \tau \dfrac{p-p'}{\tau-\tau'} u$.

Therefore $x(p-p')u = xL \dfrac{\tau-\tau'}{\tau} = xL - xL\dfrac{\tau'}{\tau}$.

And (3) becomes

$$(h-h') + (xL - x'L') - xL + xL\frac{\tau'}{\tau} = 0.$$

Therefore $\qquad (h-h') - x'L' + xL\dfrac{\tau'}{\tau} = 0.$

Therefore $\qquad \dfrac{h-h'}{\tau'} = \dfrac{x'L'}{\tau'} - \dfrac{xL}{\tau}$ ....(4).

This equation is only true when the change from the state P to the state Q is very small. But when $(\tau-\tau')$ is small $(h-h')$ is equal to the specific heat of water at temperature τ' multiplied by the change of temperature $(\tau-\tau')$, and from equation (1) of Art. 47 we see that this is equal to

$$772\{1 + 0{\cdot}000000309(\tau' - 499{\cdot}76)^2\}(\tau-\tau'),$$

or $\{772 + (499{\cdot}76)^2 \times 0{\cdot}000238548$
$- 2 \times 0{\cdot}000238548 \times 499{\cdot}76\, \tau' + 0{\cdot}000238548\, \tau'^2\} (\tau - \tau')$.

Thus we may write for convenience

$$h - h' = (k_1 - k_2\tau' + k_3\tau'^2)(\tau - \tau'),$$

and substituting this in equation (4)

$$\left(\frac{k_1}{\tau'} - k_2 + k_3\tau'\right)(\tau - \tau') = \left(\frac{x'L'}{\tau'} - \frac{xL}{\tau}\right) \ldots\ldots (5),$$

when $(\tau - \tau')$ is very small.

Next suppose the change of state from one point to another on the adiabatic to be considerable. Let the change of temperature be from τ_1 to τ_2, let the latent heat of evaporation at these temperatures be L_1 and L_2, and let the quantities of vapour in the mixture change from x_1 to x_2. To find the form which the equation (5) will take in this case we must add up on each side of the equation all the series of small quantities included between these limits, and by a process similar to that followed in finding the total heat necessary to raise liquid water from T_1 to T_2, Art. 47, we find that the sum of the three series of small quantities of form similar to those on the left-hand side of the equation is

$$k_1 \log_e \frac{\tau_1}{\tau_2} - k_2(\tau_1 - \tau_2) + \frac{1}{2}k_3(\tau_1^2 - \tau_2^2);$$

while the sum of the series of small quantities of form similar to that on the right-hand side of the equation is evidently

$$\left(\frac{x_2L_2}{\tau_2} - \frac{x_1L_1}{\tau_1}\right).$$

Thus when the change indicated is considerable equation (5) becomes

$$k_1 \log_e \frac{\tau_1}{\tau_2} - k_2(\tau_1 - \tau_2) + \frac{k_3}{2}(\tau_1^2 - \tau_2^2) = \left(\frac{x_2L_2}{\tau_2} - \frac{x_1L_1}{\tau_1}\right) \ldots (6).$$

If we consider the specific heat of liquid water to be constant, and put for its mean value 775, we shall have *instead* of (6) the simpler form

$$775 \log_e \frac{\tau_1}{\tau_2} = \left(\frac{x_2 L_2}{\tau_2} - \frac{x_1 L_1}{\tau_1}\right) \ldots\ldots\ldots\ldots\ldots (7),$$

which for most purposes is a sufficiently close approximation to the more exact equation.

The value of L is known in terms of the temperature by Art. 49, so that if the quantity of vapour x_1 in the mixture be given for that point on an adiabatic where it cuts the isothermal corresponding to τ_1, then from equation (7) the quantity of vapour x_2 can be found, which must be in the mixture when it has been expanded according to the adiabatic curve till the temperature has fallen to τ_2.

Again, when τ_1, x_1, τ_2 and x_2 are known it is possible to find from them the values of p_1, v_1, p_2 and v_2, and thus any number of points on the adiabatic may be obtained. The calculation of the form of an adiabatic in this manner is even more complicated than the exact calculation of curves of constant weight of vapour as given in Art. 52, but from numerical results of the above formulæ it has been found that the adiabatic curves also correspond very closely with an equation of the form

$$pv^n = \text{const.} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8),$$

when the quantity of vapour x in the mixture does not differ very greatly from unity.

For the value of n in this equation Rankine gives the constant quantity $n = \frac{10}{9}$ as being convenient for calculation and a sufficiently close approximation for most purposes.

Zeuner for greater exactness gives

$$n = 1{\cdot}035 + \frac{x}{10},$$

where x is the proportion of vapour in the mixture at the commencement of the expansion, and finds that the results agree very closely with those of the exact formulæ when x is not less than 0·7.

The quantity x has been spoken of as a fraction not much less than unity; in connexion with this it must be noted that the formulæ above cannot be applied in any case where the value of x becomes greater than unity, for the only interpretation which could be put upon such a value would be that the vapour had become superheated; now the formulæ of this article are true only for saturated and 'super-saturated' vapour.

54. **Comparison between curves of constant weight of vapour and adiabatics.** Take one pound of saturated steam whose pressure and volume are p_1 and v_1.

First let this steam be expanded in such a manner that the whole of it remains in the state of saturated vapour; that is to say, let the expansion be according to the curve of saturation; and let the pressure fall during the process to p_2.

By equation (7) of Art. 51 the volume must increase from v_1 to $v_1\left(\frac{p_1}{p_2}\right)^{0·9393}$.

Secondly let this steam be expanded from pressure p_1 to p_2, according to the adiabatic curve.

Since the steam is initially all in the form of saturated vapour, $x = 1$ and equation (8) of the last article takes the form

$$pv^{(1·035+0·1)} = \text{constant},$$

which may be written $p^{0·881}v = \text{constant}$.

Therefore when the pressure falls from p_1 to p_2 the volume must increase from v_1 to $v_1\left(\frac{p_1}{p_2}\right)^{0·881}$.

But $\frac{p_1}{p_2}$ is greater than unity.

Therefore $v_1\left(\frac{p_1}{p_2}\right)^{0·9393}$ is greater than $v_1\left(\frac{p_1}{p_2}\right)^{0·881}$.

So that when steam initially in the form of dry saturated vapour is expanded without gain or loss of heat according to the adiabatic curve, the volume after expansion is always less than the volume of dry saturated steam at the same *pressure.*

Therefore a portion of the steam must be condensed during the expansion.

It follows that in order to maintain the whole of the fluid under consideration in the state of saturated vapour while undergoing expansion, a certain quantity of heat must be supplied from external sources.

In the same way if a pound of fluid consisting of a mixture of water and saturated steam initially in the proportion of 3 to 7, be expanded according to the adiabatic curve, the equation giving the form of this curve will be

$$pv^{(1 \cdot 035 + 0 \cdot 07)} = \text{constant} = pv^{1 \cdot 105},$$

which may be written $p^{0 \cdot 905}\, v = \text{constant}$.

Therefore if the initial pressure and volume be $p_1 v_1$ and the final pressure p_2, the final volume will be $v_1 \left(\frac{p_1}{p_2}\right)^{0 \cdot 905}$.

Whereas if the weight of vapour in the mixture had been kept constant during the expansion the final volume would have been $v_1 \left(\frac{p_1}{p_2}\right)^{0 \cdot 9393}$ as before.

Here again the volume after expansion according to the adiabatic curve is less than the volume of a constant weight of vapour, but the difference between the two is not so great as when the whole of the fluid was initially in the state of saturated vapour, that is to say, the condensation during the expansion is less than in the case of saturated vapour.

When the proportion of vapour in the mixture is less than 0·7 of the whole the approximate formulæ do not apply, but it has been found by calculating the volumes from the more exact formulæ that the condensation caused by expansion from one given pressure to another, according to the adiabatic curve, is less as the proportion of vapour initially in the mixture diminishes, and that when the initial weight of vapour is somewhat less than half the weight of the whole quantity of fluid operated upon there is a contrary effect, some of the liquid being evaporated during any expansion according to the adiabatic curve.

These results, first arrived at by Rankine and Clausius from calculation, have since been verified by experiment.

It must be remembered that these calculations are only applicable when vapour expands against a pressure sensibly equal to its elasticity, or, what is the same thing, when the pressure does not alter suddenly from one value to a sensibly different value, but passes through all the intermediate degrees of intensity.

If the pressure alter suddenly from a greater to a less intensity the vapour will expand without doing the whole external work of which it is capable, and tend to become superheated or to evaporate any liquid with which it is mixed, if no heat be given out in the process of expansion.

This is called the "free expansion" of vapour, and may be produced by forcing it through a small orifice or a porous plug, as described in Art. 42, Chap. VI.

55. **Mixture of gases and vapours.** Let a closed vessel *A*, partly filled with liquid, have one cubic foot of space above the surface of the liquid filled with the saturated vapour of that liquid at pressure p_1, the temperature of the whole being denoted by τ.

Let another closed vessel *B*, whose total capacity is one cubic foot, contain a quantity of some different gaseous fluid at pressure p_2 and at temperature also equal to τ.

Now let the gas contained in the vessel *B* be forced into the vessel *A*, the temperature being kept constant during the process.

It is found that this does not cause any alteration of the quantity of vapour in the vessel *A*, but that the pressure upon its sides becomes equal to (p_1+p_2) by the addition of the gas.

Thus it is necessary to molecular equilibrium that a definite weight of vapour be present in each cubic foot of *space so long as* there is liquid to supply such vapour.

This weight depends only upon the temperature and is not altered by the presence of any other gas or gases in the same space.

As an exception to this rule, it was found by Regnault that the weight of vapour is somewhat increased by the presence of another gaseous substance when the two have a tendency to chemical combination.

Although the presence of another gas does not alter the ultimate state of equilibrium of a vapour, yet it materially alters both the process of attaining equilibrium and the time occupied in this process.

Thus, let a vessel A containing only a liquid and its own vapour at pressure p_1 have a communication opened with another vessel B in which there is a perfect vacuum. Then the pressure will at once fall throughout the whole liquid mass, and there will be in every part of it a sudden formation of vapour which will rush to fill the fresh space to which it now has access, that is to say, the liquid will *boil.*

The same thing will take place, though less suddenly, if there be in the vessel B a quantity of some different gas at [illegible]ure lower than p_1.

[illegible] on the other hand the vessel B contains some other [illegible] substance at a pressure equal to or greater than p_1, [illegible]n the opening of the communication between A and B [illegible] will be no fall of pressure throughout the liquid, and [illegible]fore no formation of vapour within its mass.

In this case the equilibrium of the vapour can only be [illegible]red slowly by the formation of fresh vapour at the [illegible]face of the liquid, and by its gradual diffusion among the [illegible]er gas throughout the space to which it has access,

It follows that a liquid will not boil at any given temperature unless the *total* pressure on its surface be lower than the pressure of saturation for its vapour at that temperature; [illegible] that evaporation from the surface of the liquid continues [illegible]til the pressure *caused by its own vapour* is equal to this [illegible]essure of saturation, that is to say, until the whole space [illegible]ith which it is in communication is occupied by th[illegible] [illegible]ight of saturated vapour.

56. **Conditions of ebullition.** In order that a liquid may boil, the vapour in forming bubbles in the mass of the liquid must overcome not only the pressure on the surface and that due to a certain depth of liquid, but also the cohesion of the liquid itself.

In consequence of this, if heat be applied to a liquid contained, at a given pressure p, in a vessel with a smooth inner surface, and there be little or no movement of the liquid, its temperature may be raised considerably above the temperature of saturation of vapour for the pressure p without causing ebullition, but any roughness of surface in the vessel or any considerable disturbance of the liquid makes it boil, and then vapour is given off till the temperature of the liquid is brought again to the temperature of saturation.

In ordinary circumstances water has a certain quantity of air mixed with it, but by long continued boiling, or some other processes, this air may be more or less expelled from it, and then the water may much more easily be raised considerably above the temperature of saturation for its pressure.

When water in this state does begin to boil the ebullition is very violent, and even explosive. It has sometimes been supposed, but not proved, that certain explosions of steam boilers may be caused in this way, especially where surface condensation is employed and the water thus evaporated and condensed many times successively without being exposed to the air or having an opportunity of absorbing any.

Again, when water is not pure, but contains some salt or other such substance from which the water must separate before evaporating, the temperature rises above that of saturation and remains so as long as heat continues to be applied. The important instance of this for our purpose is that of the brine which is supplied to the boilers of marine engines. Rankine gives an estimate that the boiling point of brine rises about 1·2 Fah. above that of pure water for every $\frac{1}{32}$nd of its weight of salts dissolved in it. Also that ordinary sea water contains on an average about $\frac{1}{32}$nd of its weight of salts and that the water in marine boilers should not be allowed to contain more than from $\frac{2}{32}$nds to $\frac{3}{32}$nds of *salts.*

Whatever be the temperature of the liquid, the temperature of the vapour which rises from it is always exactly the temperature of saturation for the pressure.

Hence in measuring the boiling point of water the thermometer should not be placed in the liquid but exposed to the vapour rising from it, otherwise the experiment cannot be depended on as accurate.

CHAPTER VIII.

SOME PROPERTIES OF HEAT ENGINES.

57. **Perfect elementary Heat Engine.** Looking now to machines by which the conversion of heat into external work is utilised, it will be seen from what has been said in Chap. II. that the engine which would give the simplest theoretical results would be one in which the working fluid should pass through its series of changes according to Carnot's Cycle.

Suppose any engine to obtain its heat from a source at the constant temperature τ_2 and to reject heat to a refrigerator at the temperature τ_1, also let the extreme values of the thermodynamic function of the fluid during the cycle be ϕ_1 and ϕ_2. Then since the temperature at which heat is absorbed cannot be higher than that of the source of heat, nor the temperature at which heat is rejected lower than that of the refrigerator, therefore whatever be the cycle performed the external work done cannot be greater than $(\tau_2 - \tau_1)(\phi_2 - \phi_1)$ which is the work done in a reversible cycle. Also no smaller quantity of heat can be rejected than $\tau_1(\phi_2 - \phi_1)$, and it is evident that if more heat be rejected less work must be done in the cycle.

Again, if the heat rejected be equal to $\tau_1(\phi_2 - \phi_1)$, but the work done in the cycle be different from $(\tau_2 - \tau_1)(\phi_2 - \phi_1)$, then let this work be equal to $(q - \tau_1)(\phi_2 - \phi_1)$, where q must be less than τ_2. In this case the heat absorbed from the source cannot be less than q, and therefore the ratio of the work done to the heat absorbed during the cycle cannot be greater than $\frac{q - \tau_1}{q}$, that is to say *than* $\left(1 - \frac{\tau_1}{q}\right)$.

But in a reversible cycle the ratio of the work done to the heat absorbed is $\frac{\tau_2 - \tau_1}{\tau_2}$ or $\left(1 - \frac{\tau_1}{\tau_2}\right)$, and this is greater than $\left(1 - \frac{\tau_1}{q}\right)$ since τ_2 is greater than q.

Therefore the ratio of the work performed to the heat absorbed by the engine is greatest when its cycle is reversible.

The ratio of the work performed to the heat absorbed is called the *Efficiency* of an engine.

Therefore, of all engines having the source of heat and the refrigerator at the same constant temperatures, that engine will have the highest efficiency whose cycle is reversible.

No such engine can be actually constructed, but it serves as a useful basis of comparison for the results given by other engines, and is referred to as a *Perfect Elementary Heat Engine.*

58. **Condition of Maximum Efficiency.** If there be no available source capable of supplying at constant temperature the whole quantity of heat to be absorbed during the cycle, it may be necessary for an engine to obtain different parts of its supply of heat at different temperatures.

For instance, let there be two sources at temperatures τ_2 and τ_3, capable of supplying at these temperatures the quantities of heat $\tau_2(\phi_2 - \phi_1)$ and $\tau_3(\phi_3 - \phi_2)$ respectively.

Let these quantities be represented on the diagram of energy by the indefinitely produced areas $\phi_1 AB\phi_2$ and $\phi_2 CD\phi_3$.

Suppose that the whole heat rejected by the fluid can be absorbed by a refrigerator at the constant temperature τ_1, and let EFG be the isothermal corresponding to this temperature, and cut $A\phi_1$, $C\phi_2$, $D\phi_3$ in G, F and E.

With these temperatures of absorbing and rejecting heat the highest possible efficiency would be obtained by means of two perfect elementary heat engines, one of which should perform the cycle *ABFG* and the other the cycle *CDEF*, and the combined efficiency of these two engines, that is to

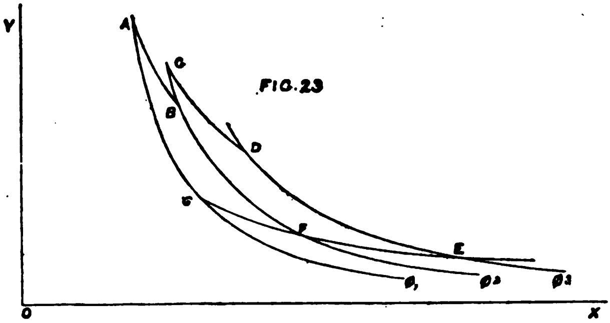


FIG. 23

say, the ratio of the whole work performed to the whole heat absorbed, would be

$$\frac{\tau_3(\phi_3-\phi_2)+\tau_2(\phi_2-\phi_1)-\tau_1(\phi_3-\phi_1)}{\tau_3(\phi_3-\phi_2)+\tau_2(\phi_2-\phi_1)}.$$

The very same result will be obtained from the single engine absorbing heat partly at the temperature τ_2 and partly at the temperature τ_3, if it perform a cycle such as that represented by *ABCDEG*, which is evidently a reversible cycle.

Therefore in this case also the condition of maximum efficiency is that the cycle of the engine should be reversible.

The same reasoning evidently applies both when there are any number of different temperatures of absorbing heat, and when there are different temperatures of rejecting heat.

Suppose then that the number of different temperatures at which heat is absorbed and rejected during a cycle be indefinitely increased, and the quantities of heat absorbed or rejected at each temperature and also the difference between two successive temperatures be indefinitely diminished.

Such a cycle may be made to differ as little as we please *from, and ultimately* to coincide with, a reversible cycle in which the temperatures of the source of heat and of the refrigerator gradually vary.

Thus in the figure let *pq*, *p'q'*, *p''q''*... be adiabatics and *pr'*, *p'r''*... and *sq'*, *s'q''*... isothermals corresponding to the temperatures τ_2, τ_2'... and τ_1, τ_1'... of absorbing and rejecting heat.

Then if the number of adiabatics drawn in the space *ABC* be indefinitely increased, and the differences of temperature $(\tau_2'-\tau_2)$... and $(\tau_1'-\tau_1)$... therefore indefinitely diminished, while the quantities of heat absorbed and rejected at each temperature also become indefinitely small, then the cycle *prp'r'p''*... *q''s'q'sq*... may be made to differ as little as we please from the cycle *ABC*, and ultimately to coincide with it.

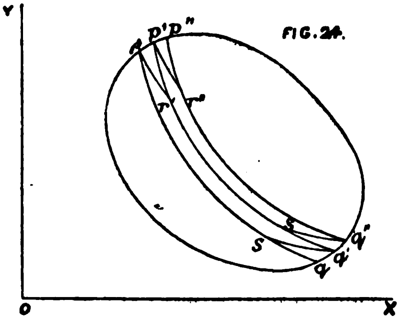


FIG. 24.

But the condition necessary that the cycle represented by *prp'r'p''*... *q''s'q'sq*... may be one which gives the maximum efficiency is that the temperatures of absorbing and rejecting heat must be equal to the temperatures of the source and the refrigerator in each operation, that is to say, that the cycle must be reversible.

Therefore also the condition that the cycle *ABC* may be such as to give the greatest possible efficiency is that it must be reversible.

And the same condition evidently holds for any cycle whatever.

59. **Regenerators.** As an instance of the variation of temperature in the source of heat and refrigerator we may mention the application to engines of what is called a "Regenerator."

Essentially this is any body which serves to absorb heat from the working fluid and thus act as a refrigerator during one part of the cycle, while it acts as a source of heat during another portion of the cycle by returning to the fluid the heat which it had before absorbed.

The usual form of a regenerator is a long chamber nearly filled with thin plates of metal, so placed as to offer as little resistance as possible to the passage of the fluid.

After receiving its supply of heat from the source, the fluid is passed from one end of the chamber to the other between the interstices of the thin plates, and has its temperature gradually reduced by giving up to the metal a certain portion of its heat.

On arriving at the other end of the chamber the fluid is passed into the refrigerator and loses such of its heat as is to be permanently rejected, after which it is again passed through the regenerator in the opposite direction, and lastly, put again into communication with the source of heat.

In the first passage through the regenerator the fluid is at a higher temperature than the metal plates and thus gives off heat, raising to the highest temperature that part of the regenerator at which it enters, and being gradually cooled down till it arrives at the other end.

In the return passage, after rejecting more heat to the refrigerator, the fluid is at a lower temperature than even the coolest part of the regenerator, and absorbs heat from the plates with which it comes in contact there.

As its temperature rises it passes forward to the other end of the regenerator, absorbing heat on its way till it passes again through the end at which it entered, where the plates are at a temperature little lower than that to which the fluid is raised by the source of heat.

It follows from Art. 58 that the most perfect results *would be obtai*ned from a regenerator in which the temperature of the metal at any point should never differ by a finite quantity from that of the fluid when passing that point. In such a case the portion of the cycle performed in the regenerator would be sensibly reversible, and the same quantity of heat which was given out by the fluid in its first passage would be absorbed in the return passage; so that the efficiency of the engine would not be less than that which would have been obtained if the cooling and heating had been effected, as in the Perfect Elementary Heat Engine, entirely by expansion and compression; such efficiency however is not obtained from actual regenerators.

The practical advantage aimed at by the employment of a regenerator is the reduction of the size of the engine necessary to perform a given quantity of work.

When the difference of temperature between the source of heat and the refrigerator is great, the cylinder of an engine must be very large if the whole change of temperature of the working fluid from one to the other is to be produced by means of expansion.

The engines to which regenerators have been applied are mostly those in which the working fluid is air, because one great objection to the employment of air engines has always been the large size of cylinder required for performing a given quantity of work.

In such engines the loss of efficiency by the use of the regenerator is estimated by Rankine at between 5 and 10 per cent. of the total heat absorbed, in the most favourable instances.

60. **Elementary Air engine.** As numerical examples, calculations are given of the results which would be obtained 1st from a perfect elementary Heat engine; 2nd, from a perfect engine with a regenerator, the working fluid in each case being air.

Let *ABCD* represent the cycle of an elementary Air engine, and let the pressures and volumes for the points *A*, *B*, *C* and *D* be p_1v_1, p_2v_2, p_3v_3, and p_4v_4 respectively.

Let ϕ_1, ϕ_2 be the thermodynamic functions for the adiabatics *AD* and *BC*.

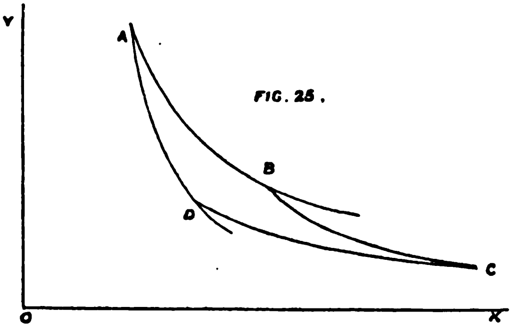


FIG. 25.

Let τ_1 the absolute temperature of the refrigerator be 550°, and τ_2 that of the source of heat be 990°, which are equal to 89·34° and 529·34° Fah.

Let the quantity of heat absorbed at the temperature τ_2 be 24750 ft.-lbs., and let p_3 the lowest pressure in the cycle be equal to the standard atmospheric pressure, namely 2116·4 lbs. per sq. foot.

In Chap. VI. Art. 40, we saw that for air

$$\frac{p_0 v_0}{\tau_0} = 53{\cdot}21 \text{ and } \gamma = 1{\cdot}408,$$

so that
$$\frac{1}{\gamma - 1} = 2{\cdot}451 \text{ and } \frac{\gamma}{\gamma - 1} = 3{\cdot}451.$$

Starting then with $p_3 = 2116{\cdot}4$ lbs., we get

$$v_3 = \frac{53{\cdot}21\,\tau_1}{p_3} = \frac{53{\cdot}21 \times 550}{2116{\cdot}4} = 13{\cdot}83 \text{ c. ft.}$$

$$p_2 = p_3 \left(\frac{\tau_2}{\tau_1}\right)^{\frac{\gamma}{\gamma-1}} = 2116{\cdot}4 \times \left(\frac{9}{5}\right)^{3{\cdot}451} = 16090 \text{ lbs.}$$

$$v_2 = v_3 \left(\frac{\tau_1}{\tau_2}\right)^{\frac{1}{\gamma-1}} = 13{\cdot}83 \times \left(\frac{5}{9}\right)^{2{\cdot}451} = 3{\cdot}274 \text{ c. ft.}$$

Again, by Art. 34, Chap. V., the heat absorbed is equal to $p_1 v_1 \log_e \frac{v_2}{v_1}$.

Therefore $p_1 v_1 \log_e \left(\frac{v_2}{v_1}\right)$ or $p_2 v_2 \log_e \left(\frac{v_2}{v_1}\right) = 24750$,

therefore $$\log_e \left(\frac{v_2}{v_1}\right) = \frac{24750}{16090 \times 3{\cdot}274} = 0{\cdot}4698,$$

therefore $$\frac{v_2}{v_1} = 1{\cdot}6 \text{ nearly} = \frac{p_1}{p_2},$$

and $$p_1 = 1{\cdot}6 p_2 = 25744 \text{ lbs.}$$

$$v_1 = \frac{v_2}{1{\cdot}6} = 2{\cdot}046 \text{ c. ft.}$$

also $$\frac{p_4}{p_3} = \frac{v_3}{v_4} = \frac{p_1}{p_2} = \frac{v_2}{v_1} = 1{\cdot}6,$$

therefore $$p_4 = 1{\cdot}6 p_3 = 3486{\cdot}2 \text{ lbs.}$$

$$v_4 = \frac{v_3}{1{\cdot}6} = 8{\cdot}64 \text{ c. ft.}$$

The heat rejected is to the heat absorbed as τ_1 to τ_2, therefore heat rejected $= \frac{5}{9} \times 24750 = 13750$ ft.-lbs.

And therefore the work done in the cycle is

$$24750 - 13750 = 11000 \text{ ft.-lbs.}$$

or $\frac{1}{3}$ of one Horse Power per stroke per minute.

The efficiency of the engine is evidently

$$\frac{24750 - 13750}{24750} = \frac{\tau_2 - \tau_1}{\tau_2} = \frac{4}{9}.$$

It will be seen that in such an engine the ratio of the greatest to the least volume is about 7 to 1, while the corresponding ratio of the least to the greatest pressure is about 1 to 12.

61. **Air engine with regenerator.** Compare with these the results given by a perfect air engine working between the same limits of temperature, absorbing the same quantity of heat and doing the same work, but performing its cycle with the help of a regenerator.

We will suppose that the volume of the air is not altered during its passages through the regenerator, and that the highest pressure and therefore the least volume of the air during the cycle are the same as $p_1 v_1$, the highest pressure and least volume in the cycle of the previous article.

Let *ABCD* represent the cycle of this engine, and as before let $p_1 v_1$, $p_2 v_2$, $p_3 v_3$ and $p_4 v_4$ be the pressures and volumes for the points *A*, *B*, *C* and *D*.

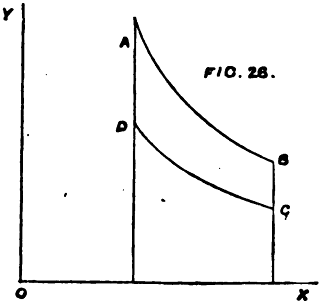


FIG. 28.

Then since by hypothesis the circumstances of absorbing heat are the same as in the last example, therefore

$$p_1 = 25744, \qquad v_1 = 2{\cdot}046,$$
$$p_2 = 16090, \qquad v_2 = 3{\cdot}274,$$

as before, and hence

$$p_3 = \frac{T_1}{T_2} p_2 = \frac{5}{9} \times 16090 = 8939; \quad v_3 = v_2 = 3{\cdot}274,$$

$$p_4 = \frac{T_1}{T_2} p_1 = \frac{5}{9} \times 25744 = 14302; \quad v_4 = v_1 = 2{\cdot}046,$$

but we saw that $\frac{v_2}{v_1} = 1{\cdot}6$.

Thus in the engine with a regenerator the greatest and least volumes are in the proportion of only 1·6 to 1, and the greatest volume is less than $\frac{1}{4}$th of the greatest volume in the cycle of an engine without a regenerator, and in which the least volume is the same.

The greatest and least pressures are in the proportion of 3 to 1.

62. **Diagrams of energy from different apparatus.** The cycles of actual heat engines are seldom if ever performed wholly in a single chamber or vessel, but whatever be the number of separate apparatus employed, the work done in each may be indicated by a diagram representing on a fixed scale the pressures and volumes of the whole mass of fluid acted upon in that apparatus.

By combining all the diagrams a figure will be obtained representing the whole work performed by the engine during the cycle.

If the weight of fluid acted on in all the apparatus be constant and equal to m pounds, then the combined diagram may evidently be considered either as the diagram of m pounds of fluid drawn to the given scale of pressures and volumes, or as the diagram of one pound of fluid drawn to the same scale of pressures but to a scale of volumes m times as large as the given scale, and isothermals or adiabatics may be drawn and compared with any of the lines of the figure accordingly.

Of course in the latter case the work done by one pound of fluid must be multiplied by m to find the work done by the whole m pounds.

Very often however the weight of fluid acted on is not the same in all the apparatus, for instance, the weight of fluid in a steam-boiler is greater than that in the cylinder.

In such cases if the weight of fluid in one apparatus be m pounds and in another apparatus n pounds, then in the combined diagram the line indicating the changes in the latter apparatus may be considered as part of the diagram of one pound of fluid to a scale of volumes $\frac{n}{m}$ times as great as the scale to which the diagram of a pound of fluid in the former apparatus is drawn.

Thus the scales of the two parts of the diagram being different, lines which are drawn as isothermals or adiabatics with reference to one part of the diagram will not necessarily have the same significance with regard to the other part of the diagram.

The area of the diagram will however still show the work done by the whole mass of fluid employed.

63. **Fluid acting as a cushion.** The difference of weight of fluid acted upon in different parts of the cycle must be produced by some portion of the fluid always remaining in one apparatus and not passing forward to undergo the same cycle of operations as the rest of the fluid.

The portion which remains in any vessel after the rest has passed forward must evidently complete a cycle of its own, independent of the remainder of the cycle of the rest of the fluid.

If this cycle could be entirely separated from that of the rest of the fluid, the diagram of any engine could be reduced to a series of diagrams of constant weight of fluid such as we have been considering.

This is not generally possible, but sometimes it can be seen from the circumstances of the case that the fluid remaining in a vessel must, during expansion, pass in a reverse order through the same or nearly the same series of changes as during compression, thus giving out no work on the whole.

In such cases the fluid is said to act as a cushion, and its diagram is easily separated from that of the working fluid, if it undergo one series of changes by itself. For let AB represent the changes undergone by the whole of the fluid, and CD the changes undergone by that portion which acts as a cushion. Through A and C draw ACK to meet OY in K, and through B and D draw BDL to meet OY in L.

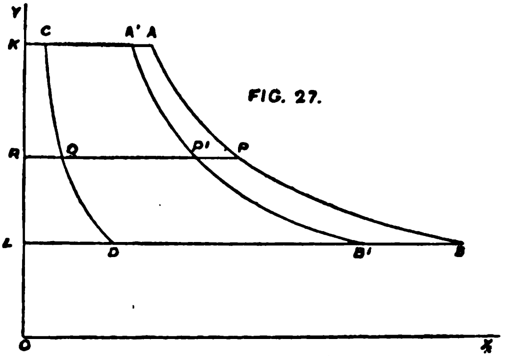


FIG. 27.

Then, by supposition, when the state of the whole fluid is represented by A, the pressure of that part which acts as a cushion is the same as when the latter is in the state represented by C. Therefore the pressure of the fluid for the point A is the same as the pressure for the point C, that is to say, the straight line AC is parallel to OX. And in the same way it may be shown that BD is parallel to OX.

Also when the volume of the whole fluid is equal to AK the volume of cushioning fluid is equal to CK.

Cutting off therefore from KA a portion $AA' = KC$, we have for the volume of the remaining or working fluid the line KA'.

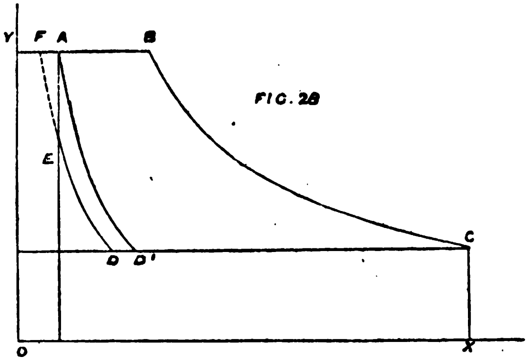
In the same way if any straight line PQR be drawn parallel to OX to cut AB, CD, KL in P, Q and R respectively, and from PR a part PP' be cut off equal to QR, the remainder RP' will be equal to the volume of the working fluid at the pressure OR.

Thus the series of changes undergone by the working fluid alone may be represented by a curve $B'P'A'$ drawn through the series of points obtained in the same way as P'. It is evident, from the construction of such a curve, that the area $KA'P'B'L$, included by it, is equal to the area $CAPBDQ$ included between the two original curves APB and CQD.

CHAPTER IX.

THE STEAM-ENGINE.

64. **Indicator diagrams.** The ideal form of the indicator diagram taken from the cylinder of an ordinary steam engine resembles that shown at *ABCDE* in figure 28. In this *A* represents the pressure and volume of the steam in the cylinder at the moment when the piston commences its stroke. At this moment the communication between the cylinder and the boiler is open and remains open until the portion *AB* of the diagram has been described, so that *AB* is a line whose form depends upon the expansion of the whole mass of fluid in the boiler as well as in the cylinder. This expansion being very small compared with the total volume of the fluid should be effected without sensible alteration of pressure, and the ideal form of the portion *AB of the diagram* is thus a straight line parallel to *OX.*



When the piston has swept through a volume equal to *AB* the communication between the cylinder and the boiler is closed, and the steam in the cylinder allowed to expand separately throughout the remainder of the stroke, this expansion being represented by the curve *BC*, after which the exhaust valve is opened and the steam allowed to escape from the cylinder.

We have supposed the cycle to be so arranged that at the end of this expansion, which is also the end of the forward stroke, the pressure shall be equal to that against which the piston is forced during the return stroke. The latter pressure is called the "back pressure," and is generally sensibly constant during that portion of the return in which the exhaust valve remains open.

Shortly before the end of the return stroke the exhaust valve is usually closed, and the small quantity of steam remaining in the cylinder is compressed by the piston during the rest of the stroke; this compression being indicated in the diagram by the line *DE*.

When the piston has arrived at the end of the stroke, the pressure and volume of the steam remaining in the cylinder being denoted by the point *E*, the communication with the boiler is again opened, and the entering steam quickly raises the pressure in the cylinder to that represented by the line *AB*.

In this operation the steam which had remained in the cylinder is of course compressed, and we may suppose its changes to be represented by the dotted line *EF*, while the fresh steam from the boiler fills up the volume represented by *FA*.

The forward stroke of the piston now recommences, and the series of operations is repeated as before.

65. **Clearance and Cushioning.** In all engines there must be some space between the end of the cylinder and the piston even when the latter is at the extremity of its stroke; also the steam-valve, or valve regulating the admission of steam from the boiler, is seldom quite close to the end of the cylinder. All the space which remains at the end of the

stroke between the piston and the steam-valve is called the "clearance." It is this space which is represented in the figure by the distance between the point *A* and the line *OY*.

In order to draw the line *OY* in its proper position with regard to the indicator diagram the clearance must be measured, but if such measurement is not to be had, the space may be taken roughly as probably equivalent to the volume swept through by the piston in from one to two inches of the stroke. The clearance should of course be taken into account in calculating the ratio of expansion during the operation *BC*, a thing which is very often neglected.

It is evident from what has gone before that the whole of the clearance is not filled with fresh steam from the boiler at each stroke, but that it is at least partly occupied by steam which had been enclosed in it when the exhaust valve was shut towards the end of the previous return stroke.

By shutting the valve at the proper point of the stroke a quantity of steam may be enclosed sufficient to fill the whole clearance at the same pressure as that of the steam from the boiler, thus producing a diagram such as that shown at *D′A*.

If we suppose the cylinder to be formed of non-conducting material the curves *D′A* and *BC* must be adiabatics, and if the temperature as well as the pressure of the steam are the same for the point *D′* as for the point *C*, then the steam which passes through the process *D′A* in being compressed, must pass in reverse order through the same series of changes during expansion, and thus corresponds exactly to our definition of cushioning steam.

In actual engines this would be only approximately the case, and when instead of passing through the process *D′A* the steam is only partly compressed by the piston as shown by the curve *DE*, it must evidently absorb heat from the fresh steam which enters from the boiler and completes the compression as shown by the dotted curve *EF*, so that this curve must be more perpendicular than an adiabatic.

In giving up the heat so absorbed, before returning to the state *E* the steam may do a certain quantity of work, and thus perform other functions besides acting as a cushion to reduce the shock to the machine in reversing the motion of the piston. That however is the principal office of this steam, and hence the name of cushioning steam is applied to it.

The curve BC indicates the changes of pressure and volume undergone by the whole mass of steam in the cylinder, but the diagram of the steam which enters from the boiler may be found very approximately by the process given in Art. 63, Chap. VIII.

For this purpose the form of the curve EF must be estimated, but generally no great error will be introduced if it be considered to coincide sensibly with an adiabatic.

After being separated from the diagram of the cushioning steam, the diagram of the working steam which enters at the beginning of each stroke from the boiler will resemble that shown at $ABCD$, (fig. 29).

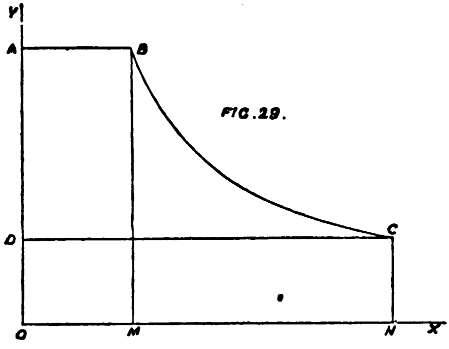


FIG. 29.

Here AB and DC represent the same volumes as FB and DC in the previous figure (fig. 28), and if BM, CN be drawn through B and C parallel to OY the ratio $\frac{ON}{OM}$ will represent the real ratio in which the working steam is expanded.

66. **Completion of the cycle.** The rejection of heat by the steam after leaving the cylinder may be effected in two ways, either by exposing it in a closed vessel called the condenser to the action of cold water, as in a condensing engine, or by allowing the steam to escape into the open air and carry off with it the whole of the heat it contains in the state *C*, as is done in a non-condensing or, as it is sometimes called, a high-pressure engine.

In the latter case the back pressure is simply the pressure of the atmosphere increased by whatever pressure is necessary to force the steam through the passages by which it leaves the cylinder.

In the former case the back pressure shown in the diagram is the pressure in the condenser, but a pump, called the air-pump, must be used to keep the condenser from being filled, and strictly the diagram of the work done by this pump should be subtracted from the diagram of the work done by the engine, but in practice it is usually included in the estimate of this work.

In whichever way the heat is rejected, a pump, called the feed-pump, must be employed to raise water from the pressure at which it was left after condensation to that of the boiler, and force it into the boiler, but the volumes of liquid water are so small that the diagram of the feed-pump could not be shown on the engine-diagram, and the small quantity of work done by this pump is also generally included in the estimate of the useful work of the engine.

This completes the cycle, which commences again by the heating and evaporation of the water in the boiler at a pressure which is sensibly constant, as shown at *AB*.

67. **Ideal condensing engine.** As an example of the application of previous results we may now find the quantities of heat which would be absorbed and rejected, and the quantity of work which would be done on the supposition that the cylinder is formed of non-conducting material, and that the steam supplied to it from the boiler is in the state of dry saturated vapour. We shall also suppose that water is returned to the boiler at the temperature at which heat is *rejected.*

Let T_1, T_2 denote the temperatures of the condenser and of the steam from the boiler, in degrees Fahr., and τ_1, τ_2 their absolute temperatures.

Then by Arts. 48 and 49, Chap. VII., the heat absorbed in raising one pound of water from T_1 to T_2 and evaporating it at T_2 is equal to

$$H_2 - h_1 = L_2 + h_2 - h_1.$$

Of these two expressions the former is the simpler, and in finding an approximate value there is a smaller error introduced by taking the specific heat of water as constant, since between 32 and T_1 the specific heat varies less rapidly than between T_1 and T_2. Using this formula then, we find for the numerical value of the heat absorbed by one pound of water, on the supposition that the specific heat of water is constant between 32 and T_1 and equal to 772,

$$H_2 - h_1 = 842872 + 235\,(T_2 - 32) - 772\,(T_1 - 32).$$

Also since the cylinder was supposed to be impervious to heat, therefore the expansion curve represented by BC (fig. 29) must be an adiabatic, and therefore during the expansion a portion of the steam will be condensed, as shown by Art. 54, Chap. VII. We shall suppose that at the end of the expansion the water thus produced falls to the temperature τ_1, along with the expanding steam. By equation (7) Art. 54, the weight of steam remaining uncondensed at the end of the expansion will be x of a pound for each pound of fluid, where

$$775 \log_e \frac{\tau_1}{\tau_2} = \frac{L_2}{\tau_2} - \frac{xL_1}{\tau_1} \text{ nearly.}$$

Therefore the quantity of heat rejected by the engine when this remaining steam is condensed is xL_1, where

$$xL_1 = \tau_1 \left\{\frac{L_2}{\tau_2} - 775 \log_e \frac{\tau_1}{\tau_2}\right\} \text{ nearly.}$$

Therefore

$$xL_1 = \tau_1 \left\{\frac{1112770 - 546\tau_2}{\tau_2} - 775 \log_e \frac{\tau_1}{\tau_2}\right\}.$$

The pressures of the steam at the temperatures τ_1 and τ_2 must be found from equation (1) of Art. 50, Chap. VII., namely

$$\log_{10} p = A - \frac{B}{\tau} - \frac{C}{\tau^2},$$

and the volumes of one pound of steam at these temperatures, from equation (6) of Art. 51, which gives

$$v = \frac{1112770 - 546\,\tau}{2{\cdot}3026\left(\frac{B}{\tau} + \frac{2C}{\tau^2}\right)p}.$$

68. **Efficiency of ideal condensing engine.** The efficiency of such an engine as we have supposed, would evidently be

$$\frac{H_2 - h_1 - xL_1}{H_2 - h_1},$$

if we take the back pressure as being due only to the pressure of condensation for the temperature T_1 and neglect the power expended in working the pumps.

In order to compare this efficiency with that of a perfect heat-engine working between the same limits of temperature we will give a definite numerical value for these limits.

Let $T_1 = 106{\cdot}34^\circ$ and $T_2 = 295{\cdot}34^\circ$.

Therefore $\tau_1 = 567$ and $\tau_2 = 756$.

Hence we have

$$H_2 = 842872 + 235 \times 263{\cdot}34,$$

thus

$$H_2 = 842872 + 61785 = 904657,$$

$$h_1 = 772 \times 74{\cdot}34 \text{ nearly} = 57391.$$

[illegible]refore the whole heat absorbed is equal to

$$904657 - 57391 = 847266 \text{ foot-pounds.}$$

Also for the heat rejected we have

$$xL_1 = 567\left\{\frac{1112770 - 546 \times 756}{756} + 775 \log_e \frac{4}{3}\right\}$$

$$= 567\{925{\cdot}918 + 775 \times 0{\cdot}2877\}$$

$$= 567\,(925{\cdot}918 + 222{\cdot}967) = 567 \times 1148{\cdot}885\,;$$

therefore $$xL_1 = 651420 \text{ nearly},$$

and $$\frac{H_2 - h_1 - xL_1}{H_2 - h_1} = \frac{847266 - 651420}{{\cdot}847266}$$

$$= \frac{195846}{847266} = 0{\cdot}231.$$

The efficiency of a perfect engine between the same limits would have been

$$\frac{\tau_2 - \tau_1}{\tau_2} \text{ or } \frac{189}{756} = \frac{1}{4} = 0{\cdot}25.$$

But we have supposed the cycle of our condensing engine to be the same as that of a perfect heat-engine in all respects, except only that the water is raised from T_1 to T_2 by heat communicated to it at the temperature T_2.

It follows that in this process there is a loss of heat equal to about 0·019 of the whole heat expended, or about $\frac{0{\cdot}019}{0{\cdot}231} = 0{\cdot}08$, which is nearly $\frac{1}{12}$th, of the heat which has been utilized in the cycle.

This loss might be avoided by condensing only a portion of the steam, and then compressing the mixture of steam and water, by means of a pump, till its temperature and pressure should be equal to that of the steam in the boiler to which it is returned, the compression being of course supposed to take place without transfer of heat.

It has been mentioned in Art. 54, Chap. VII., that if more than about half the fluid is in the state of water before the compression commences, then a farther quantity will be condensed during the process.

Hence a sufficient quantity of fluid must be left in the form of vapour to allow the compression to be completed before the whole is condensed.

69. **Expansion curves of actual engines.** In the calculations of the last two articles the expansion curve has been supposed to be an adiabatic starting from a point in the curve of saturation. In actual steam-engines this is never the case, for various reasons, some of which may be mentioned.

First, the steam at the commencement of the expansion is very seldom in the form of dry saturated vapour.

In passing from the boiler to the cylinder, the steam carries over with it a quantity of liquid water in the form of finely divided spray, which can only be got rid of by being evaporated in some way during the passage to the cylinder.

Even if a heating apparatus be employed for this purpose, the steam at the commencement of the expansion will not necessarily be free from liquid water, for the sides of the cylinder, instead of being made (as was supposed above) of non-conducting material, consist really of metal which must be at a lower temperature than the entering steam, since it has just before contained steam at the temperature of the end of the expansion in the previous stroke. The entering steam will therefore have its pressure and temperature lowered, and will be partly condensed unless it had been not only dried but considerably superheated on its way to the cylinder.

Second, whatever be the initial state of the steam, the expansion cannot follow the adiabatic curve, because the cylinder is not formed of non-conducting material.

If the motion of the piston be very slow there may be time for fresh steam to enter the cylinder until its sides are raised to the temperature, and the steam to the pressure, of the supply. In this case when the steam begins to cool by expansion, heat will flow from the metal of the cylinder, and thus the expansion curve will be less perpendicular than the *adiabatic, and* will rise above it throughout its whole length.

If, as is usual, the communication with the boiler is cut off before the sides of the cylinder have been raised to the temperature of the entering steam, then there will be a flow of heat from the steam to the metal until the two come to the same temperature, and thus during the earlier part of the stroke the expansion curve will be more perpendicular than the adiabatic, and will fall below it.

As the stroke proceeds the steam will be cooled by expansion and the metal of the cylinder heated until they both come to the same temperature. The direction of the flow of heat is then changed, for the steam continues to be cooled, by further expansion, below the temperature of the metal, and must therefore absorb instead of giving out heat.

In this way the expansion curve during the latter part of the stroke will become more horizontal than an adiabatic, and will rise above it. This alternate heating and cooling of the steam must cause a loss of efficiency, because the heat taken from the steam in the earlier part of the stroke, even if returned to it in the latter part, does not produce its full effect, but is returned only in time to be rejected by the exhaust steam.

Third, there seems generally to be a farther loss when working with steam which is in the form of saturated vapour at the commencement of its expansion, arising from the formation of water in the cylinder.

The water formed during the earlier part of the stroke and at the higher temperature, does not readily part with its heat while the steam is being cooled by expansion, and thus tends to make the expansion curve fall below the adiabatic, while at the end of the stroke the water which is expelled from the cylinder along with the exhaust steam carries away with it an undue quantity of heat.

There may be also a farther loss if some of the partially cooled water remain in the clearance space, as it will then assist the metal of the cylinder in abstracting heat from the steam which enters from the boiler at the commencement of the next stroke. The loss caused by the formation of water in the cylinder is so serious that, in order to prevent it, cylinders in which the ratio of expansion is to be considerable are provided with a "steam-jacket," or outer casing, filled with steam direct from the boiler.

By this arrangement, any water which is formed in the cylinder at the commencement of the stroke is re-evaporated by the heat supplied to the sides of the cylinder from the steam in the jacket.

Of course water is formed in the jacket, but this is allowed to drain away without interfering with the working of the engine, and it is found that a considerable economy of heat results.

The expansion curve of an engine with a steam-jacket will throughout rise somewhat above that of another engine because the temperature of the sides of the cylinder is kept higher in the one than in the other.

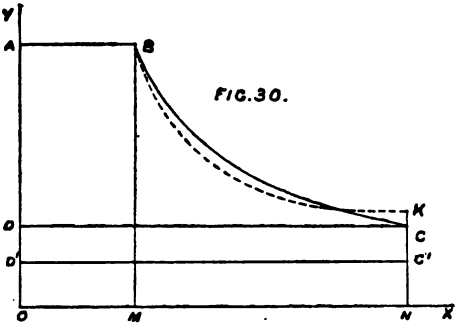
Again, in what are called "compound" engines, the steam after being partly expanded in one cylinder is transferred to another for farther expansion.

Neither cylinder of a compound engine is exposed to temperatures so different as those of the beginning and end of the whole expansion, and thus a certain amount of loss is avoided.

On the other hand, there is generally a certain loss of power during the transfer of the steam from one cylinder to the other.

70. **Approximate expansion curve.** It is sometimes assumed that an engine with a steam-jacket will have an expansion curve approximating to the curve of saturation, and that an engine whose cylinder is not steam-jacketed, but is covered with material of low conducting power, to prevent the escape of heat, will have its expansion curve approximately the same as an adiabatic.

The curves actually obtained are so different that it is scarcely worth while to use such complicated calculations as those of the curve of saturation and the adiabatic in arriving at what, after all, is only a rough approximation to the real *form.*



The simple hyperbolic curve does not differ very widely from either of these curves, and is so much more easily calculated that it is generally taken as the best approximate expansion curve.

The hyperbola is more nearly horizontal throughout than the curve of saturation, and still more than the adiabatic, that is to say, it rises above these curves.

It follows that in the earlier part of the stroke the hyperbolic curve will rise above the expansion curves of all engines except those which move very slowly indeed, or (what has nearly the same effect) work with a very small ratio of expansion.

In the latter part of the stroke, however, the expansion curves of most engines are found to rise up to, or even above the hyperbola drawn through the point of the diagram at which the expansion commenced.

Thus if *BC* (fig. 30) be an hyperbolic curve, then the usual form of expansion curve will be represented by a line somewhat resembling the dotted curve *BK*.

71. **Calculation of results from approximate expansion curve.** If we take *ABCD* as our approximation to the diagram of the working steam in an engine, separated from that of the cushioning steam, we get for the work done during the forward stroke the area *OABCN*, which is equal to the rectangle *OA* . *OM*, together with the area *MBCN*,

And for the work done against the steam during the return stroke, the rectangle $OD.ON$.

In most engines, however, the expansion of the steam is not continued till its pressure falls to that which is to be overcome during the return stroke, as this would require too large a cylinder. Therefore, after a certain amount of expansion the exhaust valve is opened and the pressure allowed to fall as suddenly as possible to equality with the back pressure.

The form of our approximate diagram will therefore be represented by $ABCC'D'$, where C is the pressure of the end of the expansion, CC' represents the sudden fall of pressure when the exhaust valve is opened, and $C'D'$ is the line of constant pressure drawn during the return stroke.

Let p_1v_1, p_2v_2, p_3v_3 be the pressures and volumes for the points B, C, C' respectively, and let $\frac{v_2}{v_1}$, the ratio of expansion, be equal to r.

Also let T_2 be the temperature of the steam in the state C at the end of the expansion, and T_4 the temperature of the feed water.

Then the work done by the steam during the forward stroke according to this approximation, is

$$p_1v_1 + p_1v_1 \log_e r = p_1v_1(1 + \log_e r) \ldots\ldots\ldots\ldots (1),$$

and if p_m be the mean intensity of the pressure throughout the forward stroke, then

$$p_m = \frac{p_1v_1(1 + \log_e r)}{v_2} = p_1 \frac{1 + \log_e r}{r},$$

and

$$\frac{p_m}{p_1} = \frac{1 + \log_e r}{r} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2).$$

Also the work done against the steam in the return stroke is p_3v_2, so that the total useful work given out is

$$p_1v_1(1 + \log_e r) - p_3v_2 \ldots\ldots\ldots\ldots\ldots\ldots (3).$$

The heat rejected may without material error be found *by subtracting* the work represented by $DCC'D'$ from the whole quantity of heat which would be rejected if the return stroke were performed according to the line *CD*.

This latter quantity of heat is called by Rankine the *heat of release*, and is evidently that which would be absorbed in raising water from the temperature T_4 to T_2, and evaporating it at that temperature.

Using the notation of Arts. 47 and 48, Chap. VII., this heat of release is therefore equal to $H_2 - h_4$, where

$$H_2 = 842872 + 235\,(T_2 - 32),$$

while h_4 may with sufficient accuracy for the purpose be put equal to $772\,(T_4 - 32)$ per lb. of steam.

Therefore the total heat rejected per lb. of steam is

$$842872 + 235\,(T_2 - 32) - 772\,(T_4 - 32) - v_2\,(p_2 - p_3) \ldots\ldots (4).$$

The heat absorbed is to be found by adding to this the quantity of heat converted into work before the release of the steam, as shown by the area *ABCD* (fig. 30), and is equal to

$$H_2 - h_4 - v_2\,(p_2 - p_3) + p_1 v_1 (1 + \log_e r) - p_3 v_2\,;$$

and since $p_1 v_1 = p_2 v_2$, this may be written

$$\text{Heat absorbed} = H_2 - h_4 + p_1 v_1 \log_e r \ldots\ldots\ldots\ldots (5),$$

and therefore the efficiency of the steam is

$$\frac{p_1 v_1 (1 + \log_e r) - p_3 v_2}{H_2 - h_4 + p_1 v_1 \log_e r} \ldots\ldots\ldots\ldots\ldots\ldots (6).$$

Rankine points out that in ordinary engines when the feed water is supplied between 100° and 120° Fahr., the numerical value of the heat of release is very nearly

$$H_2 - h_4 = 15\,p_2 v_2 \ldots\ldots\ \ldots\ldots\ldots\ldots (7),$$

from which we should get

$$\text{Heat absorbed} = p_1 v_1 (15 + \log_e r) \ldots\ldots\ldots\ldots (8),$$

$$\text{and efficiency of steam} = \frac{p_1 v_1 (1 + \log_e r) - p_3 v_2}{p_1 v_1 (15 + \log_e r)} \ldots (9).$$

72. **Modifications of indicator diagrams.** One or two matters remain to be noticed in connexion with the actual indicator diagrams of steam-engines.

Whatever be the mechanism of the engine the valve regulating the admission of steam occupies a finite time in passing between its positions of full open and absolutely closed.

During part of this time the orifice through which the steam enters the cylinder must be very small, and the pressure of the steam will thus be diminished in passing through it.

This is called "wire-drawing" the steam.

It is a case of what was mentioned in Art. 54, Chap. VII., as the free expansion of steam, and there is a tendency to cause superheating, but its effect on the diagram in properly constructed engines is too small to be noticed.

What is visible is the rounding off of the corner at B (figs. 31) and (32) between the lines of admission and expansion.

Thus the hyperbolic curve PQ fig. (32), which is to be used as an approximation to the real figure, should be drawn through a point b on the line of constant pressure Ab, corresponding to a part of the stroke rather before the steam-valve is perfectly shut.

In the same way the gradual opening and closing of the exhaust valve causes a certain rounding of the corners of the diagram at C and C', and again at D' (fig. 31).

The gradual fall of pressure about the point C is of course only produced if the exhaust valve be opened a little before the end of the forward stroke. Otherwise the expansion curve ends sharply at the end of the stroke, but the fall of back pressure about C' is even more gradual than that shown in the figures.

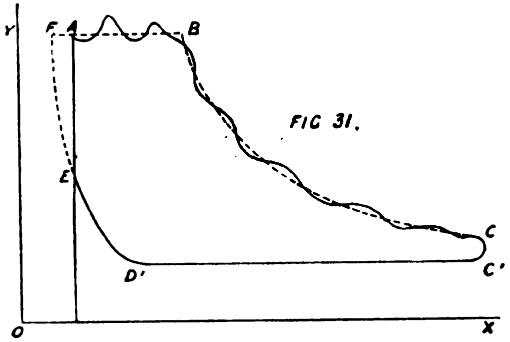
In actual diagrams there are generally also undulations in the curves, especially with fast-moving engines.

These are probably caused partly by variations in the pressure of the steam itself, but chiefly by vibrations of the *spring of the ins*trument used in taking the diagrams.

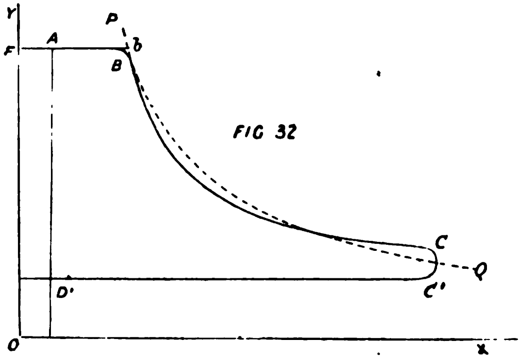
It is best to consider the true diagram as consisting of lines drawn half-way between the top and bottom of these undulations.

Thus the actual diagram of an engine may resemble the figure *ABCC′D′EA* (fig. 31).

Taking the dotted lines *EF*, *FA* to represent the operations of the entering steam in compressing the cushioning steam, the remaining dotted lines serve to show the form of the diagram when cleared of undulations.



Again, taking the diagram as shown by the dotted lines and separating the diagram of the working from that of the



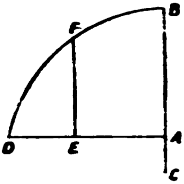
cushioning steam we get a diagram of somewhat the form shown at $ABCC'D'A$ fig. (32).

The dotted line PbQ is the hyperbolic curve, and the distance FA represents that part of the clearance which is filled at each stroke with fresh steam.

It may be mentioned here that the temperature and pressure in the condenser of an engine do not satisfy the equation $\log_e p = A - \frac{B}{\tau} - \frac{C}{\tau^2}$ of Art. 50, because there is always air in the condenser as well as steam and water, and this raises the pressure above that due to saturated vapour alone.

73. Graphic construction for $\frac{(1+\log_e r)}{r}$.

FIG. 33.



Rankine gives the following graphic construction for finding $\frac{1+\log_e r}{r}$, which may be used when tables are not at hand.

Draw any straight line AB and produce BA to C, making $AC = \frac{AB}{4}$.

From centre C with radius CB describe a circle, and through A draw AD perpendicular to AB to cut the circle in D.

Divide DA in E so that $DE = \frac{DA}{r}$, and through E draw EF parallel to AB to cut the circle DFB in F.

Then $\frac{EF}{AB} = \frac{1+\log_e r}{r}$ nearly.

And since by equation (2) of the last article

$$\frac{p_m}{p_1} = \frac{1 + \log_e r}{r},$$

therefore $\frac{EF}{AB} = \frac{p_m}{p_1}$ when $\frac{DA}{DE} = \frac{v_2}{v_1}$.

In reality $\frac{EF}{AB}$ is somewhat too large when r is large, and too small when r is small, but equal to $\frac{1 + \log_e r}{r}$, when $r = 3{\cdot}5$ nearly.

74. **The rectangular hyperbola.** Given one point on a rectangular hyperbola, any number of other points may be found graphically as follows.

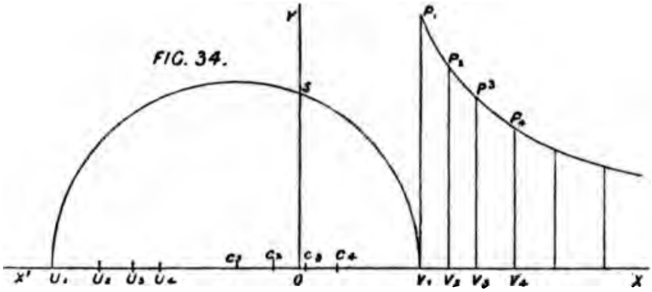


FIG. 34.

Let P_1 be the given point, draw P_1V_1 parallel to OY to to meet OX in V_1. Produce XO to X' and from OX' cut off OU_1 equal to V_1P_1. Bisect U_1V_1 in C_1, and from centre C_1 with radias C_1V_1 draw a circle cutting OY in S. In $X'X$ take any number of other points $c_2c_3c_4$... and with centres $c_2c_3c_4$... and radii c_2s, c_3s, c_4s... describe circles cutting $X'X$ in U_2V_2, U_3V_3, U_4V_4...

Through $V_2V_3V_4$ draw lines parallel to OY, and from these cut off parts V_2P_2, V_3P_3, V_4P_4... equal to OU_2, OU_3, OU_4... respectively.

Then evidently $OV_1 \times V_1P_1 = OV_2 \times V_2P_2 = OV_3 \times V_3P_3 = \ldots = (OS)^2$, and therefore $P_1P_2P_3$... are points on the hyperbola.

APPENDIX.

NAPIERIAN LOGARITHMS.

THE usual method of finding the value of ϵ the base of Napierian Logarithms and the series for the Napierian Logarithm $\log_\epsilon r$, are here given, as completing Chap. IV.

$$r^x = \{1 + (r - 1)\}^x;$$

and expanding by the Binomial Theorem we have

$$\{1 + (r-1)\}^x = 1 + x(r-1) + \frac{x(x-1)}{1.2}(r-1)^2$$

$$+ \frac{x(x-1)(x-2)}{1.2.3}(r-1)^3 + \frac{x(x-1)(x-2)(x-3)}{\underline{|4}}(r-1)^4 + \ldots.$$

which by re-arrangement can be written

$$r^x = 1 + x\left\{(r-1) - \frac{1}{2}(r-1)^2 + \frac{1}{3}(r-1)^3 - \frac{1}{4}(r-1)^4 + \ldots\right\}$$

$$+ \text{ terms involving } x^2,\ x^3 \text{ and higher powers of } x.$$

This shows that r^x can be expanded in a series beginning with 1 and proceeding in ascending powers of x; we may therefore suppose that

$$r^x = 1 + c_1x + c_2x^2 + c_3x^3 + c_4x^4 + \ldots$$

where $c_1\ c_2\ c_3\ldots$ are quantities which do not depend on x, and which therefore remain unchanged however x may be changed; also

$$c_1 = (r-1) - \frac{1}{2}(r-1)^2 + \frac{1}{3}(r-1)^3 - \frac{1}{4}(r-1)^4 + \ldots$$

while $c_2\ c_3\ldots$ are at present unknown; we proceed to find their values.

Changing x into $x + y$, we have

$$\begin{aligned} r^{x+y} &= 1 + c_1(x+y) + c_2(x+y)^2 + c_3(x+y)^3 + \ldots \\ &= 1 + c_1y + c_2y^2 + c_3y^3 + \ldots \\ &\quad + (c_1 + 2c_2y + 3c_3y^2 + \ldots)x \\ &\quad + \text{ terms involving } x^2 \text{ and higher powers of } x, \end{aligned}$$

but

$$\begin{aligned} r^{x+y} &= r^xr^y = r^y\{1 + c_1x + c_2x^2 + c_3x^3 + \ldots\} \\ &= r^y + c_1r^yx + c_2r^yx^2 + c_3r^yx^3 + \ldots. \end{aligned}$$

Since the two expressions for r^{x+y} are identically equal we may assume that the co-efficients of x in the two expressions are equal; therefore $c_1 + 2c_2y + 3c_3y^2 + 4c_4y^3 + \ldots = c_1r^y$.

But $$c_1r^y = c_1\{1 + c_1y + c_2y^2 + c_3y^3 + \ldots\}.$$

Assuming again that in these identically equal series the co-efficients of the corresponding powers of y are equal, therefore

$$2c_2 = c_1^2, \text{ or } c_2 = \frac{c_1^2}{2},$$

$$3c_3 = c_1c_2, \text{ or } c_3 = \frac{c_1c_2}{3} = \frac{c_1^3}{1.2.3},$$

$$4c_4 = c_1c_3, \text{ or } c_4 = \frac{c_1c_3}{4} = \frac{c_1^4}{\underline{|4}},$$

....

Thus $$r^x = 1 + c_1x + \frac{c_1^2x^2}{\underline{|2}} + \frac{c_1^3x^3}{\underline{|3}} + \frac{c_1^4x^4}{\underline{|4}} + \ldots$$

Since this is true for all values of x, take x such that $c_1x = 1$, or $x = \frac{1}{c_1}$; therefore

$$r^{\frac{1}{c_1}} = 1 + 1 + \frac{1}{\underline{|2}} + \frac{1}{\underline{|3}} + \frac{1}{\underline{|4}} + \ldots$$

The sum of this series is approximately equal to 2·718281828... and is generally denoted by ϵ. It is the base of the Napierian system of logarithms. We have then $r^{\frac{1}{c_1}} = \epsilon$, therefore $r = \epsilon^{c_1}$ and $c_1 = \log_\epsilon r$. That is to say,

$$\log_\epsilon r = (r-1) - \frac{(r-1)^2}{2} + \frac{(r-1)^3}{3} - \frac{(r-1)^4}{4} + \ldots$$

Again put $r = 10^x$, therefore $\log_{10} r = x$.

Now since $r = 10^x = \epsilon^{c_1}$, therefore $c_1 = \log_\epsilon (10^x)$, and therefore $c_1 = x \log_\epsilon 10$, or $\log_\epsilon r = \log_{10} r \times \log_\epsilon 10$.

Also since $10^x = \epsilon^{c_1}$, therefore $x = \log_{10} (\epsilon^{c_1})$ and $x = c_1 \log_{10} \epsilon$, or $\log_{10} r = \log_\epsilon r \log_{10} \epsilon$, but $\log_{10}\epsilon = 0·4342945$ nearly; therefore $\log_{10} r = 0·4342945 \log_\epsilon r$ and $\log_\epsilon 10 = \frac{1}{\log_{10}\epsilon} = 2·3025851$ nearly; therefore $\log_\epsilon r = 2·3025851 \log_{10} r$.

Logarithms to base ε.

N.	Log.	N.	Log.	N.	Log.	N.	Log.
1	0·00000	26	3·25810	51	3·93183	76	4·33073
2	0·69315	27	3·29584	52	3·95124	77	4·34381
3	1·09861	28	3·33220	53	3·97029	78	4·35671
4	1·38629	29	3·36730	54	3·98898	79	4·36945
5	1·60944	30	3·40120	55	4·00733	80	4·38203
6	1·79176	31	3·43399	56	4·02535	81	4·39445
7	1·94591	32	3·46574	57	4·04305	82	4·40672
8	2·07944	33	3·49651	58	4·06044	83	4·41884
9	2·19722	34	3·52636	59	4·07753	84	4·43082
10	2·30258	35	3·55535	60	4·09434	85	4·44265
11	2·39789	36	3·58352	61	4·11087	86	4·45435
12	2·48491	37	3·61092	62	4·12713	87	4·46591
13	2·56495	38	3·63759	63	4·14313	88	4·47734
14	2·63906	39	3·66356	64	4·15888	89	4·48864
15	2·70805	40	3·68888	65	4·17439	90	4·49981
16	2·77259	41	3·71357	66	4·18965	91	4·51086
17	2·83321	42	3·73767	67	4·20469	92	4·52179
18	2·89037	43	3·76120	68	4·21951	93	4·53260
19	2·94444	44	3·78419	69	4·23411	94	4·54329
20	2·99573	45	3·80666	70	4·24850	95	4·55388
21	3·04452	46	3·82864	71	4·26268	96	4·56435
22	3·09104	47	3·85015	72	4·27667	97	4·57471
23	3·13549	48	3·87120	73	4·29046	98	4·58497
24	3·17805	49	3·89182	74	4·30407	99	4·59512
25	3·21888	50	3·91202	75	4·31749	100	4·60517

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Logarithms to base ε.

N.	Log.	N.	Log.	N.	Log.	N.	Log.
1	0·00000	26	3·25810	51	3·93183	76	4·33073
2	0·69315	27	3·29584	52	3·95124	77	4·34381
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